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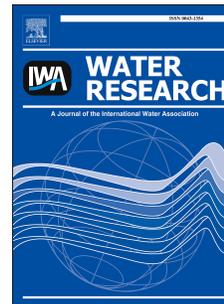
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Sewage sludge with
micropollutants (MPs)

Continuous HTL pilot reactor
325°C, 20 min

Bio-crude and MP free
aqueous and solid phase
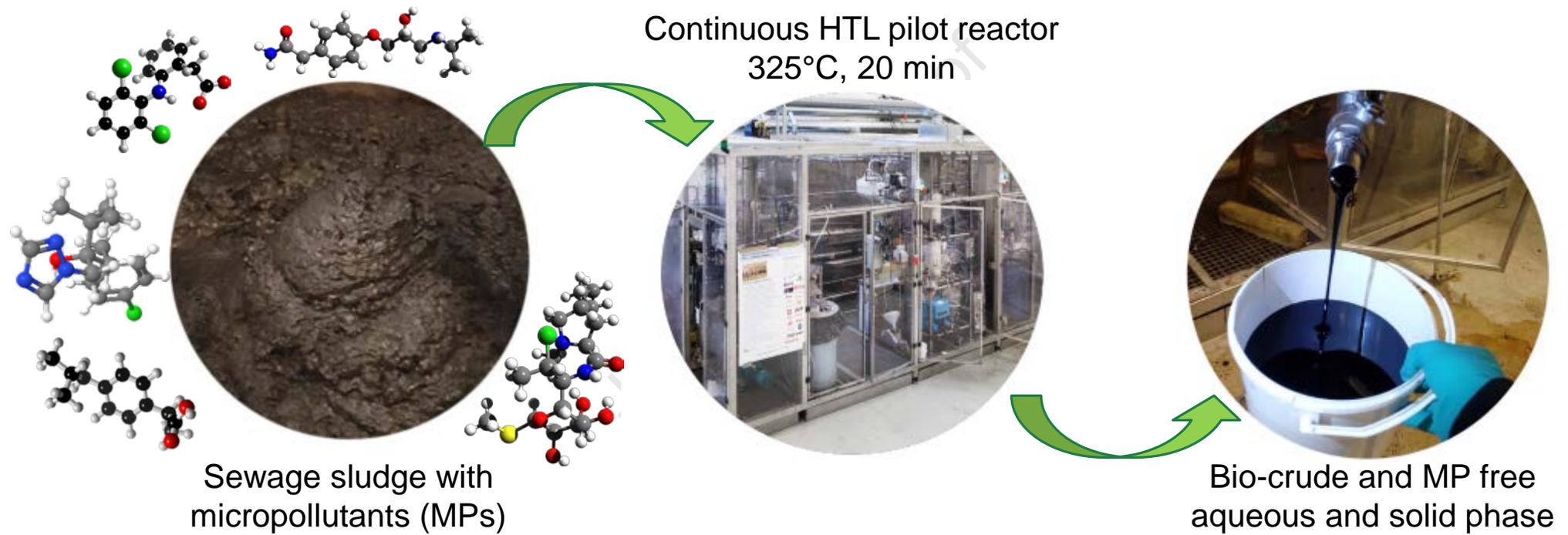
1   **Hydrothermal liquefaction of sewage sludge; energy considerations and fate of**

2   **micropollutants during pilot scale processing**

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8

9   **Abstract**

10   The beneficial use of sewage sludge for valorization of carbon and nutrients is of increasing interest while

11   micropollutants in sludge are of concern to the environment and human health. This study investigates the

12   hydrothermal liquefaction (HTL) of sewage sludge in a continuous flow pilot scale reactor at conditions

13   expected to reflect future industrial installations. The processing is evaluated in terms of energy efficiency, bio-

14   crude yields and quality. The raw sludge and post-HTL process water and solid residues were analyzed

15   extensively for micropollutants via HPLC-MS/MS for target pharmaceuticals including antibiotics, blood

16   pressure medicine, antidepressants, analgesics, x-ray contrast media, angiotensin II receptor blockers,

17   immunosuppressant drugs and biocides including triazines, triazoles, carbamates, a carboxamide, an

18   organophosphate and a cationic surfactant. The results show that a positive energy return on investment was

19   achieved for all three HTL processing temperatures of 300, 325 and 350 °C with the most beneficial

20   temperature identified as 325 °C. The analysis of the HTL by-products, process water and solids, indicates that

21   HTL is indeed a suitable technology for the destruction of micropollutants. However, due to the large matrix

22   effect of the HTL process water it can only be stated with certainty that 9 out of 30 pharmaceuticals and 5 out

23   of 7 biocides products were destroyed successfully (over 98% removal). One compound, the antidepressant

24   citalopram, was shown to be moderately recalcitrant at 300 °C with 87% removal and was only destroyed at

25   temperatures ≥325 °C (>99% removal). Overall, the results suggest that HTL is a suitable technology for energy

26   efficient and value added sewage sludge treatment enabling destruction of micropollutants.

27

28   **Keywords**: Hydrothermal liquefaction; wastewater; sewage sludge; micropollutants; pharmaceuticals;

29   wastewater treatment

30

31   **1.   Introduction**

32

33   Hydrothermal liquefaction (HTL) is a promising technology for the production of advanced liquid biofuels and

34   value-added chemicals through the conversion of a variety of organic materials. The concept involves the

35   heating of aqueous slurries at high temperatures of around 300-350 °C, at pressures over the vapor pressure of

36   water to avoid water vaporization and the accompanying latent heat of vaporization. The technology has been

37   demonstrated for a variety of wet and dry feedstocks including lignocellulosic, algae and waste (Elliott et al.

38   2015a).

39   Lately, valorization of sewage sludge by HTL has been increasingly recognized and investigated (Chen et al.

40   2020). Sewage sludge can be found in urban areas as a waste stream from wastewater treatment plants

41   (WWTPs). It represents a sustainable feedstock for HTL with low, or even negative value that shows a

42   significant biomass potential. It's production in the EU27 is approximately 11.5 MT dry matter (DM) and is

43   expected to increase to over 13 MT by 2020 (Verlicchi and Zambello 2015), in the US approximately 14 MT of

44   dry sludge is produced per year (Skaggs et al. 2018). An assessment by Seiple et al. (2017) estimated that only

45   around 50% of the sludge produced in the US is used beneficially which includes energy recovery through

46 anaerobic digestion (AD) and land application of both post-AD and non-AD sludge as fertilizer (Seiple et al.

47 2017). The rest of the sludge is incinerated for safety reasons.

48 Primary and secondary sludge are usually combined for subsequent further treatment/utilization or disposal.

49 Traditional disposal methods include landfill and incineration as well as land application for agriculture.

50 However, environmental and circular economy issues have discouraged these applications. Most advanced

51 WWTPs utilize anaerobic digestion (AD) for the further valorization and treatment of sewage sludge. AD is

52 employed in order to reduce the organic content and volume of sewage sludge while at the same time

53 recovering energy in the form of biogas (typically 60% CH_4, 40% CO_2). However, anaerobic digestion suffers

54 from very long residence times of several days to weeks, requiring large digestion tanks and produces large

55 volumes of digestate which still contains a significant proportion of carbon. Besides that, the use of digestate as

56 fertilizer has been subject to controversy due to the presence of organic micropollutants (e.g. pharmaceuticals,

57 personal care products, pesticides, hormones, etc.), which may have recalcitrant properties, becoming a hazard

58 for the entire food chain. AD has been shown to achieve only moderate reductions in pharmaceuticals and

59 estrogens (Malmborg and Magnér 2015).

60 Currently, the widespread presence of micropollutants (MPs) in aquatic systems is a major concern across the

61 globe. About 143,000 organic compounds were registered in the European market in 2012; many of which

62 would end up in water systems at some point in their lifecycle (Das et al. 2017). MPs are being detected in the

63 environment at low ng/L to µg/L levels - mostly because WWTPs are not designed to remove these compounds

64 (Ternes et al. 2004). Volatilization of MPs during any of the WWT steps is negligible due to their very low

65 Henry's constant ($<10^{-5}$ atm-m^3/mol) [7]. The biodegradable compounds (e.g. ibuprofen or caffeine), are

66 relatively easy to remove. However, a large fraction of MPs are not eliminated or biotransformed in traditional

67 WWTPs, instead they end up adsorbed on suspended particulates, i.e., on primary, secondary sludge and

68 digestate (Ben et al. 2018, Das et al. 2017).

69   HTL can offer a potential solution for tackling both the low carbon recovery and the moderate MPs elimination

70   during AD of sewage sludge. This concept has been suggested as early as the 1980's when researchers from

71   Japan published on the HTL of sewage sludge (Akira et al. 1986, Yokoyama et al. 1987), showing the conversion

72   of mixed primary and secondary sludge to bio-crude. These early reports found that yields of up to 50% could

73   be achieved on an organic basis. More recent publications have moved away from the slow heating rate batch

74   reactors employed in the 80's to using high heating rate bomb-type reactors, more alike to modern continuous

75   HTL reactors (Qian et al. 2017, 2020). For example (Madsen and Glasius 2019) reached a maximum bio-crude

76   yield of 42.2 wt.% in batch reactors at 330 °C, 10 min, and 9 wt.% solid loading of sewage sludge. Marrone et al.

77   (2018) recovered respectively 59, 39 and 49 % carbon from primary, secondary and tertiary sludge as bio-crude

78   during continuous HTL (Marrone et al. 2018), while Biller et al. (2018) recovered 64% in batch HTL reactors

79   from primary sludge (Biller et al. 2018). Subsequent upgrading of the sludge HTL bio-crude via hydrotreating

80   produces renewable fuels with high proportion of middle distillate fuels diesel and kerosene (n-paraffins) and a

81   high heating value (HHV) of around 45 MJ/kg (Castello et al. 2019) .

82   In addition, the harsh temperatures and pressures employed by HTL process can potentially aid to the removal

83   of MPs present in sewage sludge. Currently the fate of such pollutants during HTL is largely unknown. To our

84   knowledge there is only one study that has assessed the effect of HTL on bioactive compounds during HTL;

85   Pham et al. (2013) investigated the fate of estrone (estrogen), florfenicol (antibiotic) and ceftiofur (antibiotic)

86   during HTL in batch reactors at 250 and 300 °C and residences times of 15, 30 and 60 min (Pham et al. 2013).

87   The results showed complete deactivation of antibiotic resistant genes and removal of bioactive compounds at

88   reaction times over 15 min. These promising results motivated this study to assess the effect of HTL on the

89   micropollutants found in real wastewater sludge at industrially relevant processing conditions.

90   The objective of the current paper is to study the HTL of sewage sludge at realistic conditions expected in

91   industrial HTL plants in terms of residence time, heating rate and temperatures in continuous flow. The

92   continuous flow experimental conditions employed, differ significantly to previously investigated batch

93   reactors, where slow heating rates and long residence times (up to 60 mins) were used. The effect of

94   temperature on the bio-crude yield and quality is assessed and used with processing data from the HTL pilot

95   plant to optimize and evaluate the processing of sewage sludge to achieve a positive energy return on

96   investment. At the same time, the possibility of removing MPs (pharmaceuticals and biocides) in real sewage

97   sludge from an urban wastewater treatment plant is evaluated. MPs selection is based on existing

98   methodologies used to study a wide array of chemical and biological water treatment processes and not

99   necessarily a specific selection of representative compounds for HTL. Thus, unfortunately the range does not

100   cover the compounds studied by Pham et al. (2013), but the list is presently much more extensive and

101   comprising different types of pharmaceuticals, biocides and including some known transformation products

102   (see **Table S1** and **Table S2** for chemical properties). This is the first time such an industrially realistic

103   assessment on the fate of sewage sludge at different operating conditions and their effect on MPs and process

104   efficiency has been carried out.

105

106   **2. Methodology**

107   **2.1 Hydrothermal Liquefaction**

108

109   Approximately 4 m^3 of primary wastewater sludge were collected at the central wastewater treatment plant of

110   the 40,000 inhabitants town Viborg located in Bruunshåb, Denmark (operated by Energi Viborg A/S). To

111   increase the dry matter content, the sludge was filtered in a rotary vacuum drum filter, with a drum surface

112   area of 1.83 m^2. The vacuum applied varied between 0.5-1 bar and a rotational speed of 0.5 rpm was

113   employed. Previous results have shown negative energy return on investment (EROI) meaning more energy

114   input into the system than the energy obtained in the main product when low DM slurries are subjected to HTL

115 (Anastasakis et al. 2018). Higher DM slurries (approximately 20 wt.%) have been shown to increase bio-crude

116 yields and improve the overall energy efficiency during HTL (Anastasakis et al. 2018).

117 During vacuum drum filtration samples of raw sludge, filtrate and filter cake were collected and analyzed. The

118 sludge cake produced was transferred to a 1 m^3 paddle wheel mixer for homogenization and had its DM

119 content reduced from 19 % to 16 % by addition of filtrate water to optimize its pumpability. Subsequently, the

120 sludge cake was fed in the continuous HTL pilot reactor. The reactor has been previously described in detail

121 (Anastasakis et al. 2018). Briefly; the reactor has a capacity of 19 L and consists of a 140 m length tubular

122 system with a constant cross section with an internal diameter of 14.2 mm. The reactor employs a double pipe

123 counter current heat exchanger where HTL products are used to pre-heat the influent slurry. A series of electric

124 heaters are used to bring and maintain influent slurry to the desired temperature. Depressurization is achieved

125 by a hydraulic take-off system consisting of two pistons of approximately 0.5 L capacity each, working in

126 alternation. Products are collected and separated gravimetrically in a 90 L separation funnel after the

127 separation of gaseous products by a cyclone. In this study, the reactor was operated for a total of 15 h,

128 processing approximately 970 kg of slurry with a flow rate variating between, 39-94 L/h. Three different

129 temperatures were investigated: 300, 325, and 350 °C. The temperature and residence time profiles of the

130 three different temperatures investigated are depicted in **Figure 1** with the corresponding reactor sections

131 indicated. Due to technical difficulties, the flow rate was larger during the 300 °C experimental window leading

132 to a lower residence time compared to the other two experimental windows at 325 and 350 °C. The residence

133 time, bio-crude yields, energy efficiency and EROI were determined using the methods described in detail

134 previously (Anastasakis et al. 2018). Briefly, the residence time was calculated assuming that the change in the

135 density of the slurry, due to different temperatures in the reactor, follows the density of water at different

136 temperatures and pressures. The density of the feed slurry was calculated by taking into account the dry

137 matter content of the slurry and by assuming a solids density of 500 kg/m^3. The thermal efficiency (η_{th})

138 represents the energy content of the bio-crude product compared to the energy content of the feedstock in

139 terms of higher heating values (HHV) and product yield. The total energy efficiency of the system (η_{tot}) is

140 analogue to η_{th} with the addition of the external energy input to the system (in addition to the energy content

141 of the feedstock) in terms of heating and electricity. Finally, EROI expresses the ratio of the energy content of

142 the bio-crude product to the external energy supply to the main energy consuming units of the HTL system

143 (trim heater, reactor and feed pump).
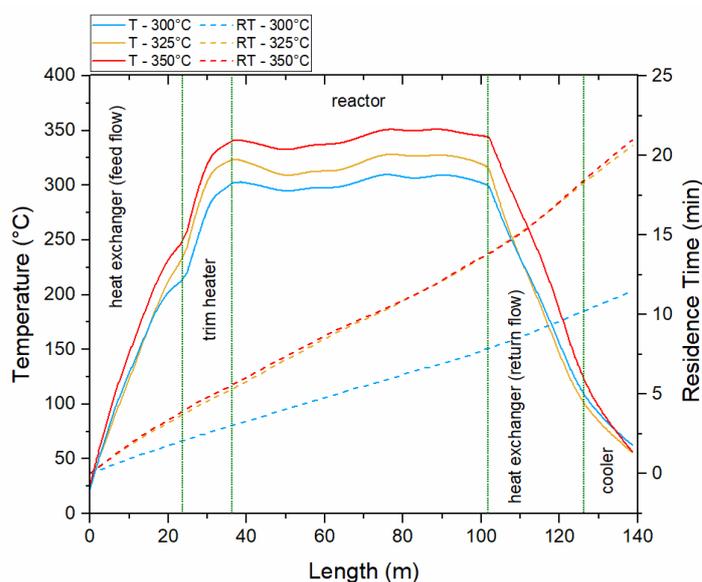
145 **Figure 1**: Temperature and residence time of the HTL reaction conditions investigated.

146

147 **2.2 Product recovery and analysis**

148

149 Once the reactor reached a steady state at the desired temperature, representative samples of bio-crude and

150 process water were collected for further analysis, samples of approximately 2 kg were collected every 45 min.

151 The process water was decanted from the bio-crude containing solids and portions of bio-crude from each

152   temperature were dissolved in methanol and vacuum filtered through a Buchner filter setup using Whatman

153   Grade 1 cellulose filter papers. Methanol was removed using a rotary evaporator (Buchi R-300, Switzerland) to

154   recover solids free bio-crude. The total amount of feedstock consumed, and bio-crude produced at steady state

155   windows of several hours at 300, 325 and 350°C were considered to determine total bio-crude yields at a given

156   temperature. The uncertainty in Table 2 is based on the deviation measured during the analyses of the samples

157   (dry matter and solids content) and on the deviation measured by the HTL control system (flow rate and energy

158   requirements).

159   Samples of sewage sludge, filtrate, filter cake, the HTL feed slurry and the HTL process water samples were

160   dried in an oven at 105 °C for 24 h to measure the DM content. The dry samples were then heated to 550 °C for

161   5 h to determine the ash content. All the samples had their elemental composition analyzed using an

162   Elementar vario MacroCube elemental analyzer (Langenselbold, Germany). The High Heating Value (HHV) of

163   the samples were calculated using the equation proposed by Channiwala and Parikh (Channiwala and Parikh

164   2002) based on their elemental composition and ash content.

165   The moisture content of the bio-crude samples was determined by volumetric Karl fisher Titration (two

166   component Hach-Lange KF1000). The ash content and elemental composition of the bio-crude samples were

167   determined using the same procedure as mentioned before taking into account the water content. All

168   measurements were repeated at least in duplicate.

169   HTL process water phase samples were analyzed for total organic carbon (TOC), COD, NH_4 and PO_4 content

170   using Merck Spectroquant cuvette tests (part numbers: TOC-114879, COD-114541, NH_4 -114559 and PO_4 -

171   114546)

172   Gas chromatography-mass spectrometry (GC-MS) was used to identify and quantify the volatile and semi-

173   volatile components of the process HTL water. The procedure includes the derivatization of aqueous samples

174   with methyl chloroformate (MCF). The method is described by Madsen et al. 2016 (Madsen et al. 2016). 200 µL

175   of the process water samples were mixed with 40 µL NaOH (5%) and 40 µL pyridine, then derivatized by adding

176   2 x 20 µL MCF. The components were then extracted by adding 400 µL chloroform containing an internal

177   standard (4-bromotoluene, 20 mg/L). To enhance the extraction and phase separation 400 µL NaHCO$_3$ (50 mM)

178   were added. A total of 30 reference standards were prepared and derivatized using the same procedure for

179   quantitative analysis making five-point calibration curves. The nonpolar phase was separated and analysed

180   using an Agilent 7890B gas chromatograph coupled to an Agilent 5977A quadrupole mass spectrometer. The

181   GC inlet was held at 280 °C with a split ratio of 20:1 and 1 µL was injected. A VF-5 ms column (60 m × 0.25 mm

182   × 0.25 µm,) was used. The column oven was programmed to start at 60 °C, hold for 2 min, ramp at 5 °C/min to

183   200 °C, ramp at 20 °C/min to 320 °C and a final hold time of 5 min. The mass spectrometer transfer line and ion

184   source were held at 300 °C. Electron impact ionization was employed at 70 eV and data was acquired in scan

185   mode (35–400 m/z).

186   High performance liquid chromatography- mass spectrometry (HPLC-MS/MS) analysis were performed for the

187   water-based samples and the process HTL solids to quantify the organic micropollutants present at the primary

188   wastewater sludge and assess which substances could be found in the process HTL products. All samples were

189   analyzed using two different HPLC-MS/MS methods, one to quantify biocides and the other for

190   pharmaceuticals and in both cases selected transformation products. The target pharmaceuticals include

191   antibiotics, blood pressure medicine, antidepressants, analgesics, x-ray contrast media, angiotensin II receptor

192   blockers, immunosuppressant drugs and other pharmaceuticals commonly found in wastewater streams

193   (chemical structures and properties are shown in **Table S1**). The target biocides include triazines, triazoles,

194   carbamates, a carboxamide, an organophosphate and a cationic surfactant (chemical structures and properties

195   are shown in **Table S2**), also found in wastewater streams. The set of target transformation products, selected

196 based on their availability to the research group due to other ongoing research activities with ozonation and

197 biological processes is presented together with the corresponding parent in the respective **Table S1** or **S2**.

198 All the samples for HPLC-MS/MS were kept at −20 °C until analysis. Before analysis, the samples were thawed

199 at room temperature and vortex shaken for 30 s. Afterwards, 1.5 mL subsamples of each sample were

200 transferred to an HPLC vial and centrifuged at 2500 RFC for 10 min. With a pipette, 1 mL of the supernatant

201 was transferred to a new HPLC vial to which 100 μL of pharmaceuticals internal standard solution (**Table S3**)

202 and 50 μL of biocides internal standard solution (**Table S4**) were added. Finally, 10 μL of the aqueous samples

203 were injected into the HPLC system. The remaining supernatant in the centrifugation vial was discarded and

204 the remaining pellet was further extracted. Solid samples, both the thawed solids, as well as the pellets were

205 simply extracted by a two-step process, first water, second methanol, using an ultrasonic bath. Solid samples

206 were weighted into 4 mL vials, 3 mL water was added and the vial was ultrasonicated for 15 min, followed by

207 centrifugation (2500 RFC for 10 min) and further collection of the supernatant. Afterwards, the procedure was

208 repeated but this second time using 3mL methanol. Pellets were extracted directly in the HPLC vial using the

209 same approach, but in this case only 1.5mL of the solvent were used. With a pipette, 1 mL of the different

210 supernatant was transferred to a new HPLC vial to which 100 μL of pharmaceuticals internal standard solution

211 (**Table S3**) and 50 μL of biocides internal standard solution (**Table S4**) were added. Finally, 10 μL of the extracts

212 were injected into the Agilent 1200 Series binary LC gradient HPLC system (Agilent Technologies, Santa Clara,

213 CA, USA) which was coupled to a 5500 QTRAP (ABSciex, Framingham, MA, USA) triple quadrupole mass

214 spectrometer. For both methods, a Synergy Polar RP column was used, and the gradient elution consisted of

215 water and methanol, both containing 0.2% formic acid (v/v). The remaining methodological conditions were

216 specific for each method and further detailed in the supplementary information. Analytical figures of merit are

217 shown for the pharmaceuticals and biocides method in **Table S5** and **Table S6**, respectively. The concentration

218 of the OMPs was calculated by linear regression of standard calibration (1/x weighting) by SCIEX OS v1.5

219 software. Concentrations reported for the water samples reflect the total content, meaning a sum of what was

220 measured in the water phase and extracted from the respective pellet.

221 Removal rate was calculated based on the mass balance of the HTL system:

$$Removal\ (\%) = \frac{m_{in} - (m_{W,out} + m_{S,out})}{m_{in}} \times 100$$

222 Where, m_{in} is the mass of pollutant fed to the system; $m_{W,out}$ is the mass of pollutant in the residual water

223 phase; $m_{S,out}$ is the mass of pollutant in the residual solid phase. The amount of pollutant in the gas and bio-

224 crude phase was considered negligible. When the compounds were not detected in the residual water or solid,

225 the respective LOD was used to estimate the mass but if the compounds was detected then LOQ was used

226 instead.

227

228

229 **3. Results and Discussions**

230 **3.1 Filtration process**

231

232 **Table 1** shows the DM and ash content of the filtration fractions of the vacuum drum filter. The untreated

233 sewage sludge had a DM content of 3.5 wt.%. The drum filter generated a slurry cake with 19.3 wt.% DM,

234 which was adjusted to 16 wt.% using the filtrate water to obtain a slurry which had optimal pumping

235 performance in the HTL reactor. The vacuum drum filtration process was able to remove a large quantity of ash

236 from the sludge. The initial ash content of 13 wt.% was reduced to 7 wt.% in the filter cake while it increased to

237 50 wt.% in the filtrate. This is most likely due to the presence of soluble salts in the liquid filtrate fraction.

238 Reducing the ash content in the cake is beneficial for further processing as it increases the amount of organic

239   material fed to the reactor per volume, makes product separation easier to perform and also results in lower

240   ash content in the final bio-crude.

241

242

243   **Table 1**: analysis of sludge samples

|	Sewage Sludge	±	Cake / HTL feed slurry	±	Filtrate	±
Dry matter (wt.%)	3.5	0.6	19.3[c]	1.5	0.2	0.03
C[a] (%)	43.1	0.04	45.3	0.56	36.1	0.35
H[a] (%)	7.3	0.04	7.8	0.08	6.8	0.16
N[a] (%)	2.5	0.01	3.0	0.36	3.5	0.21
S[a] (%)	0.3	0.02	0.3	0.03	0.6	0.02
O[a, b](%)	33.7	0.06	36.5	0.15	2.9	0.32
Ash* (%)	13.0	0.80	7.0	0.60	50.0	0.60
HHV (MJ/kg)*	19.9	0.07	21.1	0.13	19.3	0.35

244   [a]*Dry matter based.* [b]*Calculated by difference.* [c]*Feed slurry dry matter was reduced to 16% for processing*

245

246   **3.2 Hydrothermal Liquefaction**

247   **3.2.1   Bio-crude analysis**

248 During the experimental campaign three different temperatures were investigated 300, 325 and 350 °C. A total

249 of over 65 kg of bio-crude was produced and representative samples were taken from each temperature for

250 further analysis. **Figure 2** shows the elemental analysis of the three bio-crudes with the calculated HHV and ash

251 content. Due to the removal of solids from the bio-crude via filtration, the ash content is low ranging from 1

252 wt.% at 300 °C and 325 °C to 2 wt.% at 350 °C. The ash content of bio-crude is important to consider as it is

253 undesirable for further processing especially for catalytic hydrotreatment and has to be removed either in the

254 HTL reactor inline or post reaction. Marrone et al. (2018) for example, achieved an ash content from

255 continuous processing of primary sludge of 0.38 wt.% using inline filtration (Marrone et al. 2018). A clear trend

256 in increasing HHV can be observed with increasing temperature, resulting in a maximum at 350 °C of 34.5

257 MJ/kg, this is primarily due to the reduction of oxygen from 22.1 to 12.7 wt.%. There is an increase in nitrogen

258 content observed with increasing temperature from 300 to 325°C from 2.5 to 3.2 wt.%, which is similar to the

259 content at 350 °C. The nitrogen content observed in the bio-crudes are comparatively lower to e.g. (Conti et al.

260 2020) and (Marrone et al. 2018) who report nitrogen levels of 4.3-5.1 and 5.0-5.6 wt.% respectively. However,

261 sourced wastewater treatment sludge for both cases also had higher amounts of nitrogen present in the

262 feedstock 3.6-7.9 and 7.4 wt.% respectively compared to the 3.0 wt.% in the current study (See Table 1).The

263 bio-crudes are comparable in oxygen contents to typical HTL bio-crudes produced from other biomasses which

264 are commonly in the region of 10-15 wt.% (Madsen and Glasius 2019). The current results of around 14 wt.%

265 oxygen for the 325 °C and 350 °C are within the upper range of published data from primary sludge batch and

266 continuous processing (5-15wt.% oxygen) (Marrone et al. 2018, Mujahid et al. 2020, Qian et al. 2020). The

267 results show that there is a combined heteroatom content of N and O between 24.6 and 15.7 wt.% which

268 requires significant upgrading in a bio-crude post processing stage such as hydrotreating. Overall the bio-

269 crudes are characterized by a high solid content before filtration (See **Table 2**), but equally have already been

270 shown from previous campaigns to be suitable for further upgrading after ash removal via catalytic

271 hydrotreatment to produce fuels with very low heteroatom content (Castello et al. 2019).
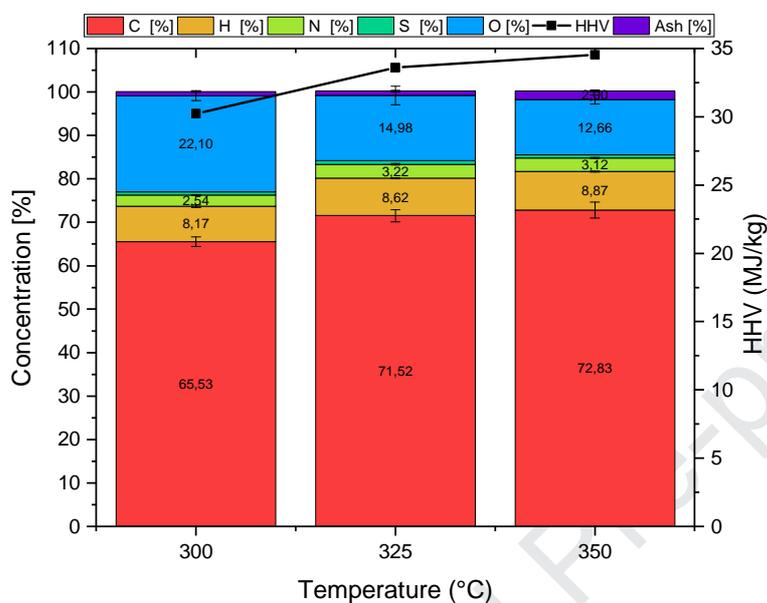
272

273 **Figure 2**: Elemental analysis and HHV of bio-crudes produced at different temperatures

274

275

276   **3.2.2   HTL process energy evaluation**

277

278 The continuous pilot scale HTL reactor allows constant monitoring of the energy input provided to the heating

279 elements in the trim heater and the main reactor section. For each temperature a window of 1 h was defined

280 to analyze the processing data and experimental results from bio-crude characterization. The results are

281 summarized in **Table 2** for a representative 1 h window each. The energy in the feedstock is calculated from

282 the flow rate, dry matter content of the slurry and the HHV of the dry sludge. The bio-crude yield ranged from

283 28 wt.% at 300 °C to a maximum of 64 wt.% at 325 °C. However, taking the solids and moisture content of the

14

284   bio-crudes into account, the highest bio-crude yield of 41 wt.% was obtained at 325°C. This broadly confirms

285   the results presented by Madsen and Glasius (2019) where the optimum processing conditions for primary

286   sludge was identified in batch reactors as 330 °C, 10 min residence time yielding 42.2 wt.% bio-crude (Madsen

287   and Glasius 2019). At 325 °C the bio-crude also exhibited a relatively high HHV of 33.6 MJ/kg which resulted in

288   the highest thermal efficiency (chemical energy recovery) of 69%, in relation to the feedstock HHV and yield.

289   Taking into consideration the amount of energy required to heat the reactor (7.5 kW) and pumping the slurry

290   to the required pressure (0.4 kW) a total efficiency of 57% was achieved. When purely comparing the amount

291   of energy produced as bio-crude (26.3 kW) to the input energy for heat and pumping, the energy returned on

292   energy invested (EROI) for the reactor can be calculated. This results in a ratio of 3.4 for the 325 °C experiment

293   meaning 3.4 times more energy is produced as bio-crude than is invested for processing. This ratio drops to 2.2

294   at 300 °C and 1.6 at 350 °C. In a previous publication using the same feedstock and reactor at 350°C but with a

295   very low dry matter content of the slurry of only 4 wt.% vs. 16 wt.% in the current study, an EROI of 0.5 was

296   achieved. This highlights the importance of high dry matter slurries for continuous HTL processing also due to

297   the fact that the bio-crude yields are significantly higher with 53 wt.% vs 25 wt.% (prior solids removal)

298   (Anastasakis et al. 2018). From a processing efficiency point of view, the data in **Table 2** suggests that

299   processing at 325 °C is most suitable, even though the oxygen content in the bio-crude is slightly higher than at

300   350 °C. Due to the similar carbon content of the bio-crude at 325 and 350 °C but the greater yield at 325 °C

301   there is more carbon found in the bio-crude fraction, which is consistent with the process water analysis

302   presented in **Table 3**. It has to be highlighted that the flow rates in the reactor were not constant making the

303   comparison of different temperatures difficult. However, flow rates and hence residence times were

304   comparable for the experiments at 325 °C and 350 °C (43 and 39 L/h, respectively). Future campaigns will aim

305   to highlight the effect of temperature and flow rate (residence time) independently by keeping one parameter

306   constant. Nevertheless, the data shows that a positive EROI is possible at all three temperatures but

15

307 considerable optimization opportunities exist by carefully adjusting the operating conditions to optimize the

308 interchanging effects of temperature, residence time on the product yields and quality as well as the energy

309 requirements for the reactor to operate. Finally, it should be noted that the EROI calculations only take into

310 consideration the energy requirements of the HTL plant in terms of heat and pumping, not auxiliary equipment

311 power, filtration of the sludge and any transportation of sludge.

312

313 **Table 2**: Energetic analysis of HTL sludge processing at different experimental conditions.

Temperature	°C	300	±	325	±	350	±
Flow rate	L/h	94	0.3	43	0	39	0
Dry matter content	(wt.%)	16.0	1.4	16.0	1.4	16.0	1.4
Feedstock consumed	(kg, dry)	15.0	1.4	6.9	0.6	6.3	0.6
Energy in Feedstock	(kW, dry)	82.7	7.5	37.9	3.3	34.5	3.0
Bio-crude yield (as received)	(wt.%)	28.1	0.4	64.1	0.9	53.4	0.8
Bio-crude yield (dry)	(wt.%)	23.6	0.5	53.0	1.1	45.5	1.0
Bio-crude yield (dry solids free)	(wt.%)	17.7	0.5	40.8	1.2	31.8	0.9
HHV bio-crude (dry solids free)	(MJ/kg)	30.2	0.6	33.6	0.2	34.6	0.4
Energy in Bio-crude (dry solids free)	(kW, dry)	22.3	3.1	26.9	3.2	19.2	2.5
Thermal efficiency (η_{th})	(%)	27.0	1.3	69.3	2.4	55.6	2.2
Trim heater energy requirements	(kW)	6.9	0.6	5.5	0.3	7.4	2.4
Reactor energy requirement	(kW)	2.3	>0.01	2.0	0.3	4.2	0.1
Main pump energy requirement	(kW)	0.86	NA	0.40	NA	0.36	NA
Total efficiency (η_{tot})	(%)	24.1	1.2	57.4	2.2	41.2	0.4
EROI		2.2	0.2	3.4	0.2	1.6	0.1

314

315

3.2.3 HTL process water analysis

317

When implementing a HTL system for sludge valorization the fate of the resulting aqueous phase is an important factor to consider. As shown in **Table 3**, the COD concentrations of the samples range 40-50 g/L, which is two orders of magnitude higher than a typical wastewater treatment influent concentration (typically 200-800 mg/L). It is therefore troublesome to simply divert the HTL process water stream back to the WWTP influent. Although the volumes are relatively low compared to the overall inflow, the concentrations are very high, making other treatment options more attractive. The most commonly suggested options for this are anaerobic digestion and catalytic hydrothermal gasification (CHG). Both technologies have their advantages and disadvantages. AD suffers from typically long residence times, inhibition of the process by certain organics and low overall COD conversion (~60%) (Tommaso et al. 2015). Catalytic hydrothermal gasification has the advantage of low residence times, very high COD conversions (~99%) but suffers from the required catalyst being poisoned by sulphur (Elliott et al. 2015b, Marrone 2016). Both technologies also perform more efficiently at high carbon leadings due to the fact that more energy can be recovered from higher carbon concentrations per volume. The levels found in HTL process water of around 20 g/L are low if thermally efficient process water cleanup is to be performed by AD or CHG. The analysis of the process waters in **Table 3** shows similar compositions amongst the different temperatures. The TOC value is around 20% lower for the 325 °C produced water sample. This fits with the high bio-crude yields observed at this temperature where more carbon is fractionated to the bio-crude. The data further shows that the ammonium concentration increases with temperature as well as the N-containing pyrazine compounds. The employed GC-MS method is not complete and only the largest peaks were quantified when authentic standards were available. Other compounds that

337   were present, exhibiting large peak areas, which are not quantified are 3-methoxy-pyridine and acetone.

338   Overall, the data demonstrates the need to further cleanup of this process water while some of the identified

339   compounds pose a threat to biological treatment due to the inhibitory or recalcitrant nature.

340

341   **Table 3**: Bulk analysis of HTL process waters.

mg/L	300 °C	±	325 °C	±	350 °C	±
Total Organic Carbon (TOC)	20,000	100	15,700	200	20,200	850
Chemical Oxygen Demand (COD)	50,833	438	42,250	250	51,850	50
NH_4^+	373	3	635	5	720	5
PO_4^{3-}	4.3	NA	2.3	NA	7.6	NA
Acetic acid	454.3	113.3	698.7	80.6	446.0	42.2
Isobutyric acid	14.4	1.3	13.9	1.9	15.0	3.8
Pyrazine	358.6	29.8	378.4	19.8	451.0	61.0
Pyrazine, methyl-	330.4	16.0	350.5	27.1	372.8	44.6
2-Cyclopenten-1-one, 2-methyl-	55.6	8.7	73.6	6.9	63.1	6.2
Pyrazine, 2,5-dimethyl-	5.4	0.4	6.4	0.7	6.1	0.8
Malonic acid	13.6	1.6	10.4	6.5	1.4	0.1
Pyrazine, ethyl-	7.0	0.5	2.6	3.5	4.8	4.6
Pyrazine, 2,3-dimethyl-	5.8	0.6	7.1	0.9	6.8	1.1
Methyl Malonic acid	9.1	0.9	11.0	1.1	11.3	1.1
2-Cyclopenten-1-one, 3-methyl-	140.6	16.5	213.8	20.5	219.9	25.4
Levulinic acid	19.2	2.0	16.2	2.7	18.7	2.7
Pyrazine, trimethyl-	4.3	0.3	5.4	0.5	4.9	0.5

Succinic acid	56.1	7.0	51.1	9.3	39.8	11.7
Pyrrolidinone	27.6	0.6	30.8	1.3	31.0	1.2
3-Hydroxypyridine monoacetate	20.8	27.1	7.8	0.8	7.2	0.9
Glutaric acid	7.9	0.3	8.9	0.9	7.2	0.8
Phenol	7.3	1.0	7.0	0.9	6.0	1.2
Pyrocatechol	71.8	16.2	57.6	0.4	57.4	0.6

342

3.3 Organic micropollutants

344

345 The results from both the pharmaceuticals (**Table S7**) and the biocides (**Table S8**) analysis indicate similar

346 behavior for both type of organic micropollutants. The overall trend indicates the presence of several

347 compounds in the sewage sludge fed to the HTL system as well as on the respective drum filtrate water and

348 slurry fed to the HTL. Regarding the pharmaceuticals, 11 of the 36 parent compounds analyzed and 12 of the

349 16 known transformation products were not detected in the sewage sludge and HTL slurry. Thus, a total of 25

350 pharmaceuticals (azithromycin, clarithromycin, erythromycin, roxithromycin, ciprofloxacin, clindamycin,

351 sulfamethizole, trimethoprim, atenolol, metoprolol, propranolol, carbamazepine, citalopram, diclofenac,

352 ibuprofen, tramadol, venlafaxine, iomeprol, valsartan, irbesartan, candesartan, mycophenolic acid, oxazepam,

353 benzotriazole and gabapentin) and 4 transformation products (alpha-hydroxymetoprolol, *O*-

354 demethylmetoprolol, (10S,11S)-dihydroxy-10,11-dihydrocarbamazepine and diclofenac amide) were present

355 with quantifiable levels in the slurry fed to the HTL. Two of the x-ray contrast media, iohexol and iopromide,

356 known as hydrophilic could only be determined in the drum filtrate but not on the sludge/slurry.

357 Concentrations in the sludge and HTL slurry ranged from LOQ (clindamycin, *O*-demethylmetoprolol) up to 131

358   µg/kg for losartan, in line with the levels (0.01 – 5000 µg/kg) reported in the literature for the different

359   compounds (Lindholm-Lehto et al. 2018).

360   Out of 16 biocides tested, only 7 were detected and/or quantified, tebuconazole, carbendazim, diflufenican

361   and its transformation product (TP) 2-[3-(trifluoromethyl)phenoxy]pyridine-3-carboxylic acid (known as AE-B)

362   and the cationic surfactant benzalkonium chloride (also known as alkyldimethylbenzylammonium chloride /

363   ADBAC) in its different even-numbered alkyl chain lengths 12-BAC, 14-BAC and 16-BAC. Concentrations were

364   very different between the type of compounds. Tebuconazole and carbendazim were in similar ranges (0.1 to

365   10 µg/kg) to those reported previously for sewage sludge (Chen et al. 2012, Kupper et al. 2006). AE-B was only

366   detected in the different samples, and diflufenican was in similar levels to tebuconazole and carbendazim. For

367   the best of our knowledge, diflufenican has been reported previously in streams and potentially linked with

368   effluent discharges (Muenze et al. 2017) but never directly quantified in sewage sludge. The levels of

369   benzalkonium chlorides were much higher (100 – 5000 µg/kg) than for the other biocides. Benzalkonium

370   chlorides belong to the broader family of quaternary ammonium compounds, a major class of cationic

371   surfactants, used as the ingredients in fabric softeners, antistatics, disinfectants, biocides, detergents, phase

372   transfer agent and numerous personal care products (Zhang et al. 2015). Benzalkonium chlorides are known to

373   sorb to sludge in wastewater treatment plants and the values presently found are within the orders of

374   magnitude previously reported (µg to mg per kg of sludge) (Zhang et al. 2015). The analytical method was not

375   extensively optimized for the solids extraction thus the values shown should not be considered as absolute but

376   indicative of their order of magnitude.

377   After the HTL treatment both residual water and solids were analyzed. The HTL process water, most probably

378   due to the higher organic content than typical wastewater, presented a significant matrix effect leading to

379   significant ion suppression for some of the pharmaceutical and biocide compounds. It should be noted that this

380   ion suppression effect is not observed for typical wastewater (Table S5), and was not observed for the extracts

381 from the HTL solids. Therefore, for the compounds for which isotope dilution measurements are possible due

382 to availability of the respective internal standard, the removal is unquestionable (**Table 4**). In addition, the HTL

383 solids revealed no detectable level of compounds for both pharmaceuticals and biocides. It can, thus, be clearly

384 stated that the HTL was capable of removing 9 out of the 30 pharmaceutical compounds measured in the HTL

385 feed: azithromycin 99.8%, clindamycin 83.7 – 84.8%, atenolol 98.8 – 98.9%, citalopram 86.7 – 99.9%, diclofenac

386 98.7-98.8%, ibuprofen 98.4 – 98.5%, iomeprol 99.7%, losartan 99.9% and mycophenolic acid 99.8%. Regarding

387 the biocides, 5 out of the 7 compounds were also effectively removed: tebuconazole 99.3 – 99.4%, diflufenican

388 99.9%, 12-BAC 99.9%, 14-BAC 99.9% and 16-BAC 99.9%. Removals above 98% were the most common. The

389 exception was clindamycin that was only detected in the feed (thus the removal rate calculation is only based

390 on the limits of the analysis, not necessarily of the process) and citalopram that presented a removal rate

391 dependent of the temperature. We presently demonstrate that several other micropollutants can be removed

392 above 98%, besides the previously studied estrone, florfenicol and ceftiofur [13]. It should be noted that HTL

393 presents high removal for compounds that are usually recalcitrant to other treatment processes: for instance,

394 diclofenac presents very limited removal by biological processes and requires advanced oxidation processes

395 (Beltrán et al. 2009) or ibuprofen that is easily biodegraded but recalcitrant to ozonation (Quero-Pastor et al.

396 2014).

397 Carbamazepine, tramadol, venlafaxine, valsartan, irbesartan, candesartan, oxazepam, gabapentin, alpha-

398 hydroxymetoprolol, *O*-demethylmetoprolol, (10S,11S)-dihydroxy-10,11-dihydrocarbamazepine and diclofenac

399 amide) seem to be also removed in the HLT, but lack confirmation by an internal standard. The compounds

400 that were affected by the ion suppression problem (clarithromycin, erythromycin, roxithromycin, ciprofloxacin,

401 sulfamethizole, trimethoprim, metoprolol, propranolol, and benzotriazole) in the process water matrix did not

402 reveal any peak, but conclusions cannot be drawn. For the biocides, carbendazim suffered ion suppression in

403 the HTL water samples, thus it can only be confirmed that it is not present in the HTL solids after the treatment.

404   AE-B seems to be totally removed, the compound was not detected in either the HTL process water or solids,

405   but lacks confirmation by an internal standard.

406   A very limited number of compounds seem to be partly recalcitrant to HTL process. Citalopram was quantified

407   in the HTL water from the 300 °C process, but not for the higher temperatures (325 and 350 °C). The same

408   seems true for benzotriazole and the transformation product alpha-hydroxymetoprolol. These findings suggest

409   that 300 °C might not be sufficiently high temperature or/and the residence time was too short (approximately

410   10 min RT at 300 °C compared to 20 min at 325 °C and 350°C) for the efficient elimination of the

411   aforementioned compounds. Further attention should be paid to the formation of transformation products.

412   We observed the potential formation of 5-amino-3-methylisoxazone in the process water, not fully confirmed

413   by an internal standard and not easy to explain once the respective parent compound sulfamethoxazole was

414   not measured in the feed (Table S7). Nevertheless, isoxazole rings (azole, five-membered nitrogen heterocyclic

415   ring, with an oxygen atom next to the nitrogen) are commonly found in a number of antibiotics and pesticides

416   (Chen et al. 2018) thus, other potential parent compounds might be present in the feed. It should be stressed

417   that the current targeted transformation products are based on the pre-existing knowledge from other type of

418   chemical and biological systems. Thus, there is a need for future studies to clarify the removal pathways and

419   potential formation of transformation products in HTL.

420   All in all, the HTL technology reveals a big potential to cope with the contamination by organic micropollutants.

421

422   **Table 4:** Removal rate of pharmaceuticals and pesticides in the hydrothermal reactor at the different

423   temperatures, based on the mass balance of the system

Group	Compound	HTL 300 °C Removal %	±	HTL 325 °C Removal %	±	HTL 350 °C Removal %	±
Antibiotics	Azithromycin	99.8	<0.1	99.8	<0.1	99.8	<0.1

	Clindamycin	84.3	<0.1	85.4	0.1	85.3	<0.1
Blood pressure regulators	Atenolol	98.8	<0.1	98.9	<0.1	98.9	<0.1
Antidepressant / Analgesic	Citalopram	86.7	<0.1	99.9	<0.1	99.9	<0.1
	Diclofenac	98.7	<0.1	98.8	<0.1	98.8	<0.1
	Ibuprofen	98.4	0.1	98.5	0.1	98.5	0.1
X-ray contrast media	Iomeprol	99.7	<0.1	99.7	<0.1	99.7	<0.1
Angiotensin II receptor blocker	Losartan	99.9	<0.1	99.9	<0.1	99.9	<0.1
Other uses	Mycophenolic acid	99.8	<0.1	99.8	<0.1	99.8	<0.1
Triazoles	Tebuconazole	99.3	0.1	99.4	0.1	99.3	0.1
Carbamates	Carbendazim	98.8	<0.1	98.9	<0.1	98.9	<0.1
Carboxamide	Diflufenican	99.9	<0.1	99.9	<0.1	99.9	<0.1
Cationic surfactant	12-BAC	99.9	<0.1	99.9	<0.1	99.9	<0.1
	14-BAC	99.9	<0.1	99.9	<0.1	99.9	<0.1
	16-BAC	99.9	<0.1	99.9	<0.1	99.9	<0.1

424

425

4. Conclusions

427

Overall this work has shown that hydrothermal liquefaction is a suitable technology for beneficial use of sewage sludge due to several advantages that can be concluded from this study:

- A positive energy return on investment is possible by processing sewage sludge at sufficient dry matter content with modern continuous flow HTL reactors, producing around three times more energy in the bio-crude than is required for pumping and heating.

23

433 - The highest bio-crude yields are obtained at 325 °C, broadly agreeing with batch literature data. At this

434 temperature the highest EROI is also achieved, while the bio-crude quality is slightly superior at 350 °C.

435 - The process waters are very high in COD (~50 g/L), requiring further treatment and also introducing a

436 large matrix effect for organic micropollutants analysis.

437 - At least 9 out of 30 pharmaceuticals and 5 out of 7 biocides are removed with over 98%. – Whether

438 other compounds are being removed needs to be tested after analytical method adaption/cleanup.

439

440

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442

443 **5. Acknowledgments**

449 **6. References**

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532

Highlights:

- Pilot scale HTL of sewage sludge performed at 300, 325 and 350°C
- Maximum bio-crude yield of 41% obtained at 325°C
- Bio-crude produced contained 3.4 times more energy than used for HTL processing
- Large matrix effect of HTL process water on micropollutant analysis encountered
- All quantifiable micropollutants were successfully destroyed at and above 325°C

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: