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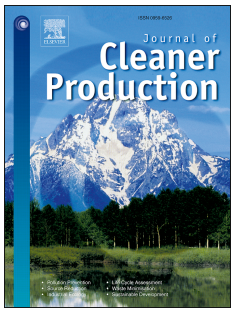

Energy valorization of integrating lipid extraction and hydrothermal liquefaction of lipid-extracted sewage sludge

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Credit Author Statement

Y. Fan and A. Hoffmann designed and performed the experiments, and analyzed the data. Y. Fan and F.G. Fonseca calculated the energetic efficiency and wrote discussion. Y. Fan wrote the manuscript in consultation with M. Gong, U. Hornung and N. Dahmen. U. Hornung and N. Dahmen supervised the project, and put efforts to revise the manuscript. All authors discussed the results and commented on the manuscript.

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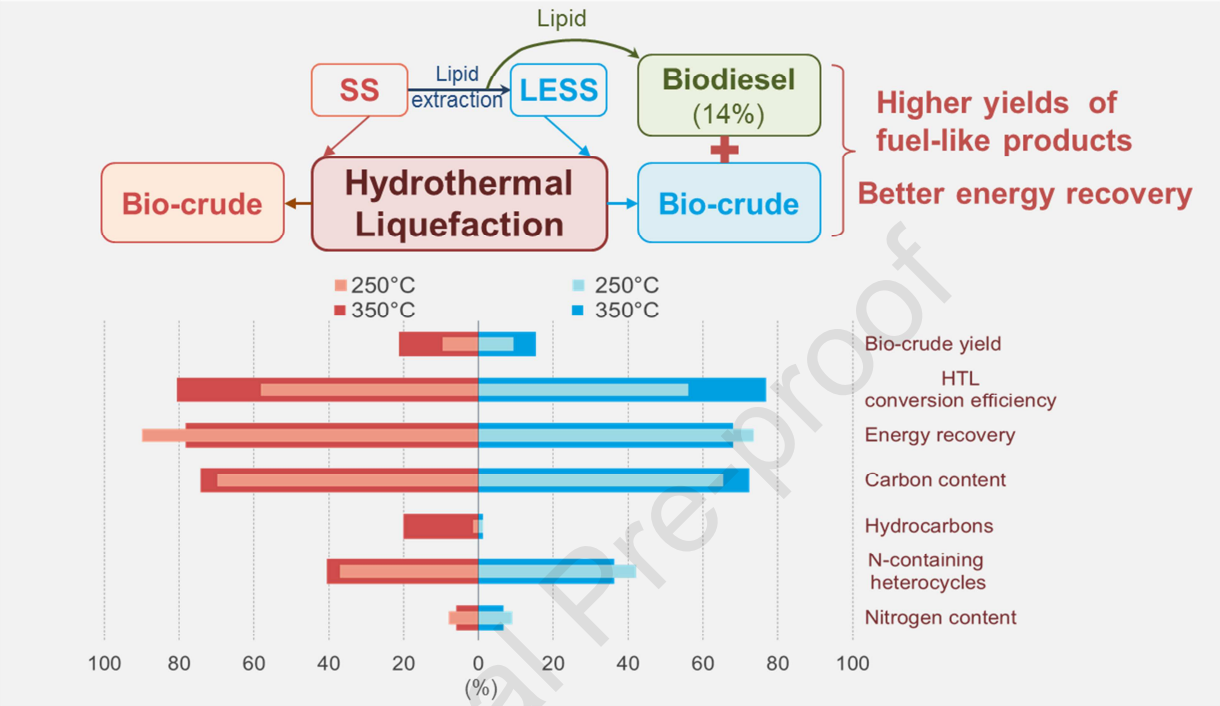
Graphical Abstract



Energy valorization of integrating lipid extraction and hydrothermal liquefaction of lipid-extracted sewage sludge

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Abstract

With the rapid growth in population and urbanization, a development in sustainable treatment of sewage sludge has become an urgent environmental concern globally. Lipid extraction has been investigated in order to valorize waste sewage sludge treatment through a pathway that leads to biodiesel. In this work, an integrated approach that combines lipid extraction of sewage sludge with hydrothermal liquefaction of the lipid-extracted sludge was studied in order to maximize valorization. The hydrothermal process was performed at temperatures ranging from 250 to 350 °C with 20 min. Regarding the bio-crude: below 300 °C, similar values are found with and without lipid-extraction, with the former variant containing more nitrogenated compounds stemming from Maillard reactions, while the latter more hydrocarbons; at 350 °C, higher bio-crude is obtained from raw sewage sludge owning to the conversion of lipids. Palmitic acid was selected as a model lipid to elucidate the role of lipids during the process, as well as to provide an improved understanding of the reaction network. Energy recovery reached values of 85.4 % for hydrothermal liquefaction of sewage sludge and 98.3 % for integrated approach considering the whole range of biofuel products. The energy consumption ratio was applied to estimate energetic efficiency for the combined process, making it possible to estimate the breakeven point of the process, plus the efficiency of both the hydrothermal process on its own in comparison with the combined option.

Keywords: sewage sludge; lipid extraction; HTL; biocrude; energy; Energy consumption ratio

1 Introduction

Regarding sewage sludge (SS), a multitude of technologies has been proposed to substitute traditional ways of disposal. Research has reported that landfills, composting and combustion not only waste material but also create environmental problems (Cai et al., 2004; Syed-Hassan et al., 2017). In addition, initiatives for the reduction of CO_2 emissions drive society to find alternative sources to supply an ever-increasing demand for fuel products, providing an opportunity to view sewage sludge, not as a waste, but rather as a source of carbon and energy. Therefore, sewage sludge is considered a very promising waste feedstock, due to its availability, as well as to its organic matter and nutrient contents (Gherghel et al., 2019; Peccia and Westerhoff, 2015).

In order to meet the globally growing energy demand and support climate mitigation strategies, the attention to make energy recovery from widespread waste has been increasingly paid to disposal of sewage sludge. Biodiesel production from SS is increased in recent years, because the production of biodiesel from vegetable oils has faced shortcomings associated with high feedstock prices, and competition with edible crops for arable land use has limited the expansion of production capacity (di Bitonto et al., 2020; Kwon et al., 2012). Sewage sludge may be considered a cost-effective alternative due to its availability and lipid content, typically in the range of 20 wt.% (dry ash-free basis) (Zhu et al., 2014); the lipid extraction potential can reach up to 12 wt.% of the dry sludge (Supaporn and Yeom, 2016). The lipid content present in sewage sludge typically consists of free fatty acids in the range of C10 to C18 as precursors for the production of esters (typically methyl esters, FAME) (Siddiquee and

Rohani, 2011). Different methodologies can be applied for the conversion and extraction of lipids from sewage sludge. Lipids may be extracted using conventional liquid-liquid methods from raw sludge prior to methanolysis, or the reaction can take place directly on dry sludge or dewatered sludge. Assuming an overall yield of FAMEs of 7.0 wt.% with respect to the dry sludge, Dufreche et al. (Dufreche et al., 2007) reached a breakeven price of 0.83 $\$\cdot L^{-1}$, for which drying the dewatered sludge (80 – 85 wt.% water) was considered the most energy and cost-demanding step. Mondala et al. (Mondala et al., 2009) estimated the price of biodiesel to be 0.85 $\$\cdot L^{-1}$ from in situ transesterification of dewatered sludge at an assumed yield of 10 % FAMEs/dry weight of sludge. Pokoo-Atkins et al. (Pokoo-Aikins et al., 2010) reported a value of 0.76 $\$\cdot L^{-1}$, by extracting lipids from the dry sludge prior to methanolysis. These values are comparable to those reported for petro-diesel and show the high potential of sewage sludge as a competitive lipid source for the production of biodiesel.

Recently, research is being focused on the performing extraction of lipids from wet sludge that avoids energy-intensive drying steps. Pastore et al. (Pastore et al., 2013) carried out hexane extraction directly on dewatered sludge followed by methanolysis of extracted lipids, reaching to 18 wt.% FAMEs with the lowest energy demand 17 $MJ\cdot kg^{-1}$. Olkiewicz et al. (Olkiewicz et al., 2014) porposed the direct sequential liquid–liquid extraction using hexane for lipids is feasible and compares well with those classical pre-drying methods, 27 % (dry sludge) lipids ws obtained under the optimized extraction. Kech et al. (Kech et al., 2018) further tested the extracting efficiency of different solvents to the direct lipid-lipid extraction of lipids for biodiesel production, alternative solvents including cyclohexane/isopropyl

alcohol improved the yields of lipids. However, the residual sludge (lipid-extracted sewage sludge, LESS) must be effectively employed to achieve favorable energy balances and production costs.

During the last decade, hydrothermal liquefaction (HTL) is considered one of the most promising technologies, as it is able to convert high-moisture feedstocks to an energy-dense liquid biocrude, which could be further refined into transportation fuels. (Fox et al., 2019; Kruse and Dahmen, 2018). HTL typically takes place at medium temperature ranges from 250 °C to 370 °C, the operating pressure is between 4 and 22 MPa, and reaction time 10 – 60 min (Rao et al., 2018). The yields of biocrude from sewage sludge are influenced by operation parameters, type of catalysts and solvents. From previous studies of sewage sludge using HTL, the biocrude produced varies from 10 to 48 wt.% (Qian et al., 2017; Suzuki et al., 1988; Wang et al., 2018). Currently, some physical and chemical methods for sewage sludge pre-treatment were studied. Chen et al. (Chen et al., 2020) explored the influence of microwave power on yield and composition of bio-crude from HTL of SS, where increasing the microwave power can improve the biocrude yields by between 2 – 10 %. Kapusta (Kapusta, 2018) reported that the ultrasound pretreatment can achieve 19 % increase bio-crude from HTL of SS 320 °C compared with un-treated sludge. Co-liquefaction SS with other types of feedstocks has attracted considerable research interest as it aims to increase biocrude yield with improving quality (Yang et al., 2019). Fox et al. (Fox et al., 2019) conducted the hydrothermal co-liquefaction of food waste and SS after 200 °C pretreatment. To the best of our knowledge, limited information is available considering the integration of

HTL and lipid extraction. Based on the success in using LESS as anaerobic digestion feedstock (Olkiewicz et al., 2014), and the proven feasibility of using lipid-extracted algae residue (Frank et al., 2012; Shahi et al., 2020; Vardon et al., 2012) and de-oiled yeast (Chopra et al., 2019) in HTL, the integration of both these processes is attractive due to the maximum utilization of sewage sludge, as well as the different products obtainable. When disregarding the water content, LESS is mostly comprised of proteins and carbohydrates. In particular, proteins have been confirmed to promote to bio-crude production using HTL (Posmanik et al., 2017). Maillard reactions play a significant role in the bio-crude product distribution and composition, which is caused by the reaction of amine groups present in proteins with carbonyl groups present in reducing carbohydrates (Fan et al., 2018; Zhang et al., 2016).

Therefore, the objectives of this paper are: 1) to quantify and characterize the extracted lipids from sewage sludge and to evaluate their applicability for biodiesel production; 2) to investigate the hydrothermal conversion efficiency of LESS through HTL, comparing the different products generated by HTL of SS and LESS in order to evaluate whether LESS can be a potential feedstock for the production of fuel components; 3) to reveal the effect of lipids on bio-crude products based on model compounds with an improved understanding to reaction pathways; 4) to estimate the coupling effect of lipids extraction and HTL of LESS, in terms of the yields of fuel-like products and process efficiency.

2 Materials & methods

2.1 Materials

Digested sewage sludge (SS) was obtained from a wastewater treatment plant (WWTP) in Plieningen, Stuttgart, Germany. The SS sample was collected from the WWTP and stored at -18 ºC until use. The sludge was used directly as received (moisture content 78.75 wt.%) in this work. Crude protein was determined by Kjeldahl method, carbohydrates was determined by using the phenol-sulfuric acid photometric estimation by DuBois method (Jimenez et al., 2013).

Methanol, sodium bicarbonate, sodium chloride, and palmitic acid (PA) were supplied by Sigma-Aldrich, analytical grade. Supelco 37 Component FAME Mix used as a standard solution was purchased from Restek. The same supplier provided HPLC grade dichloromethane (DCM), tetrahydrofuran, and hexane.

2.2 Lipid extraction and quantification

Extraction was carried out in a Soxhlet apparatus using hexane mixed with ethanol as a solvent (1:1 vol.%) (Zhu et al., 2014). For practical operation, 5 g of dried sample were poured in the thimble and 90 mL solvent mixture was placed in the still pot. Extraction was performed at a temperature that ranged from 70 to 80 °C and sustained for about 6 h. After extraction, the mixed solvent was removed using a rotary evaporator at 40 °C under vacuum at 50 mbar. Then, the remnant lipid fraction was stored in a desiccator overnight and weighed the next day to determine the extraction yield. The left residual was air-dried and defined as lipid-extracted sewage sludge (LESS).

In-situ transesterification of sewage sludge was conducted by reactive extraction by adapting the method presented by Mondala et al. (Mondala et al., 2009), which goes as follows: 2 g of freeze-dried sludge was weighed into a 250 ml flask. The sludge samples were then treated at 75 °C, 5 ml (5 vol.%) H_2SO_4, and 24 ml methanol (mass ratio of methanol to dried sludge (12:1)). 25 ml of hexane was added to improve the lipid solubility in the reaction mixture. The sludge was then suspended in a solution using a magnetic stirring bar and the mixture was heated to the set temperature using a hot water bath with a retention time of 8 h. After the reaction was stopped, the mixture was allowed to cool, and the flask contents were transferred into a 100 ml bottle. Then, 2.5 ml of saturated NaCl solution and 25 ml of hexane were added. The mixture was then centrifuged at 3000 rpm for three minutes and the supernatant hexane phase was withdrawn and transferred into a 100 ml round-bottom flask. The extraction procedure was repeated three times. Afterward, the total volume of the collected supernatant was washed with 5 ml of a 2 % (w/v) sodium bicarbonate solution and the aqueous phase was allowed to settle. The upper layer passed through a filter paper containing anhydrous sodium sulfate before being collected.

FAME content in the hexane phase was analyzed using a Shimadzu GC-FID (Agilent 7890 B). A Stabilwax-DA, 30 m × 0.25 mm × 0.25 mm column was used for the analysis. The column temperature was programmed to start at 40 °C, to be maintained for 10 min, and then to be increased from 40 to 250 °C for 10 min at 8 °C/min. The sample injection volume was 1.0 µl, with a split ratio of 10:1. Injection of standard solutions (Supelco 37 Component FAME Mix) with distinct concentrations and examination of the linear regression of the responses aided

155 determination of the linearity. For example, the linear correlation coefficients were 0.99857
156 for palmitic acid (C16:0) (y = 0.87773489 x – 14.148712) and 0.99876 for stearic acid (C18:0)
157 (y = 0.88245915 x – 8.9711545). Construction of the analytical curves enabled us to describe
158 the mathematical equations used for quantitation and calculations.

159 **2.3 Hydrothermal liquefaction**

160 Each sample was liquefied in micro-autoclaves with a volume of 24.5 ml made of stainless
161 steel (1.4571 Ti), which can withstand pressures of up to 40 MPa and a maximum temperature
162 of 400 °C.The reactors were loaded with sludge slurry, 25 wt.% (dry-free basis). It should be
163 noted that the lipid-extracted sludge was mixed with water to achieve similar conditions to
164 dewatered sludge. For the case of palmitic acid, each batch consisted of 10 wt.%. The
165 micro-autoclaves were flushed to remove the undesired air and then pressurized to 2 MPa
166 using nitrogen gas. Heating was performed in a gas chromatography (GC) furnace at a heating
167 rate of 40 K/min and kept at the target temperature (250, 300, or 350 °C) for 20 min. After the
168 reaction, the autoclaves were taken out of the oven and put in cold water to cool down and to
169 stop the reaction. All the experiments were executed in triplicates to assess standard deviation
170 (error bars in figures).

171 *Product separation and analysis*

172 After the HTL reaction, the micro-autoclaves were opened in a gas-tight containment after
173 flushing air out using nitrogen. The gas composition was measured by manually injecting
174 100 µl of the gas sample in an Agilent 7890A gas chromatograph (equipped with a 2 m
175 Molsieve 5 Å and 2 m Porapak Q column). The mixed products including aqueous phase,

bio-crude and solid residue were washed with dichloromethane (DCM) and filtered through vacuum filtration using a Whatman nylon membrane (47 mm, 0.45 μm pore size). Most of the bio-crude remained stuck to the micro-autoclave walls after the reaction, so additional use of DCM was required to maximize the recovery of products. The solid residue remaining in the filter was placed in an oven and dried overnight at 105 °C to determine the dry weight. The biphasic mixture obtained (aqueous product plus bio-crude) was centrifuged and separated. The organic solvent was evaporated by flushing with nitrogen for 24 h. Once a constant weight had been achieved, it was recorded and considered as the bio-crude mass.

The C, H, and N contents of the bio-crude and the solid residue were measured using a Vario EL III analysis system (Elementar Analysensysteme GmbH, Hanau, Germany). Oxygen content was calculated by difference.

GC-MS analysis of bio-crude was carried out using an Agilent 6890N gas chromatograph with an Agilent 5973 MSD mass spectrometry detector and a DB-5 capillary column (30 × 0.25 mm × 0.25 μm) after diluting with tetrahydrofuran (1:1 ml/ml) and filtering with a 0.20 μm polytetrafluoroethylene (PTFE) Filter. The substances were identified using the NIST library, considering only molecules with a match quality above 80 %. The amount of the different compounds was estimated by the relative area percentage method.

Thermal gravimetric analysis (TGA, Mettler toledo DSC 822) approximately 10 mg of the samples was measured within the range from 20 to 800 °C with a heating rate of 10 K/min and N_2 flow rate of 50 ml/min, to apply a method devised by Liu et al. (Liu et al., 2018) for the assessment of the fractionation potential of produced bio-crude in a petroleum refinery

197 environment. The total carbon (TC), total organic carbon (TOC), total inorganic carbon (TIC),
198 and total nitrogen (TN) in the aqueous phase were measured with a Dimatec® 2100
199 instrument. Ammonium (NH_4^+), nitrate (NO_3^-), and nitrite (NO_2^-) were investigated by
200 Metrohm 838 advanced sample processor device. Organic acids were analyzed with an
201 Aminex HPX-87H column (Biorad, Hercules, CA, USA).

202 **2.4 Data definition**

203 The yields (Y_i) of the different product fractions were calculated as the weight of the
204 recovered mass of organic matter in the product (OM_i) related to the total mass of organic
205 matter in the feedstock (OM_{feed}, daf.), see Eq. (1).

$$Product\ Yields\ \ (wt.\%) = \frac{OM_i}{OM_{feed}} \times 100 \quad (1)$$

206 The HTL conversion efficiency was calculated as the difference in feedstock mass (OM_{feed})
207 and solid residue (OM_{SR}) (assuming this to be unconverted feedstock) related to the feedstock
208 mass (OM_{feed}), as shown in Eq. (2).

$$HTL\ conversion\ efficiency\ (\%) = \frac{OM_{feed} - OM_{SR}}{OM_{feed}} \times 100 \quad (2)$$

209 The elemental distribution, namely carbon distribution (CD) and nitrogen distribution (ND)
210 are defined as the amount of an element in the product (m_{Ei}) relative to the amount in the
211 feedstock product (m_{Efeed}), see Eq. (3).

$$Elemental\ Distribution\ \ (wt.\%) = \frac{m_{Ei}}{m_{Efeed}} \times 100 \quad (3)$$

212 Higher heating value (HHV; $MJ \cdot kg^{-1}$) was estimated using the modified Dulong's formula
213 (Posmanik et al., 2017) as given in Eq. (4).

$$HHV(MJ/kg) = 0.0338 \times C + 1.428(H - O/8) \quad (4)$$

214 The energy recovery (ER) as the sum of the higher heating values (HHV_i) of the recovered
215 fuel-like products (bio-crude, bio-char, when necessary, extracted lipids) weighed by their
216 yield Y_i^* relative to the value (HHV_{feed}) of the dry feedstock, see Eq. (5).

$$ER\ (\%) = \frac{\Sigma\ (Y_i^* \times HHV_i)}{HHV_{feed}} \times 100 \quad (5)$$

217 The concept of ECR (Energy Consumption Ratio, Eq. (6)), was employed by Sawayama et
218 al. (Sawayama et al., 1999) and Minowa et al. (Minowa et al., 1998) to estimate the energetic
219 viability of the process by relating the heat demands of the process to the heating value of the
220 products. Values lower than 1 indicate a good energetic balance, revealing that the energy
221 content of the products (E_0) is higher than the energy requirement of the production process
222 (E_L).

$$ECR = \frac{E_L}{E_0} \quad (6)$$

223 For the case of hydrothermal liquefaction, the authors propose the following formula (Eq. (7)),
224 for which w_i is the water content, $c_{p,w}$ is the specific heat of liquid water (4.18 kJ·kg^{-1}·K^{-1}), $c_{p,s}$
225 is the specific heat of dry solid (1.25 kJ·kg^{-1}·K^{-1}), ΔT is the temperature difference to ambient
226 temperature (25 °C), Y_i is the product yield (wt.% daf.), and w_0 is the organic fraction of the
227 feedstock sludge (wt.% daf.).

$$ECR_{HTL} = \frac{E_L}{E_O} = \frac{\left[w_i c_{pw}\,\Delta T + (1 - w_i) c_{ps}\,\Delta T\right](1 - r_2)}{[(1 - w_i) Y_i (HHV) w_O] r_1} \quad (7)$$

228 For the complete process chain, the concept of ECR was extended to additional process steps
229 (Eq. (8)), which make use of heat demands (Q_i) and product energy potentials (E_i). Four
230 different process configurations were considered: 1) HTL to produce only bio-crude (ECR_{BC}),
231 which employs Q_{HTL} and E_{BC}; 2) HTL to produce bio-crude and solid residue as energy

carriers (ECR_{BC+SR}), which employs Q_{HTL}, $E_{BC,}$ and E_{SR}; 3) considering HTL products and lipid extraction ($ECR_{BC+SR+L}$), which employs Q_{HTL}, Q_{drying}, $Q_{extraction}$, E_{BC}, $E_{SR,}$ and E_{LIPID}; 4) considering HTL products and FAME production from the lipids extracted ($ECR_{BC+SR+FAME}$), which employs Q_{HTL}, Q_{drying}, $Q_{extraction}$, $Q_{methanolysis}$, E_{BC}, $E_{SR,}$ and $E_{FAME.}$

$$ECR = \frac{E_L}{E_O} = \frac{(\sum Q_{step})(1 - r_2)}{(\sum E_{product})r_1} \quad (8)$$

The efficiency of combustion (r_1) and the efficiency of heat recovery (r_2) can be adjusted depending on the technology employed. Sawayama et al. (Sawayama et al., 1999), in 1999, used values for r_1 and r_2 of 0.6 and 0.5, respectively. On the other hand, more up-to-date values of 0.7 and 0.5 have been proposed by Vardon et al. (Vardon et al., 2012) and an optimized hypothetical case using state-of-the-art combustion and heat recovery technology may permit reaching values of 0.9 and 0.6 (Demirbas, 2009). The latter two situations are considered during the discussion of results, and are named the case A and case B, respectively. As per Eq. (9) (Sawayama et al., 1999), Q_{HTL}, the heating demand of the hydrothermal liquefaction process was estimated as the sensible heat required to increase the temperature (ΔT) of the mixture (water + dry sludge) to the target temperature. No phase change was assumed to take part during the HTL process.

$$Q_{HTL} = w_i c_{pw} \Delta T + (1 - w_i) c_{ps} \Delta T \quad (9)$$

For the case of drying (Eq. (10)), a final temperature of 100 °C was assumed with $\Delta H_{vap,w}$ as the heat of vaporization of water (2.26 MJ·kg^{-1}) and HHV_s as the higher heating value of the sludge.

$$Q_{drying} = \left[w_i(\Delta H_{vap,w} + c_{pw} \Delta T) + (1 - w) c_{ps} \Delta T\right] \quad (10)$$

$Q_{extraction}$ was assumed to be 60.95 $MJ \cdot kg^{-1}_{lipid}$ taken from Olkiewicz et al.(Olkiewicz et al., 2012), and a value of 934 Btu/lb (2.17 $MJ \cdot kg^{-1}$) was obtained for the demand of the methanolysis process ($Q_{methanolysis}$) given by Huo et al. (Huo et al., 2009). A value of 39.5 $MJ \cdot kg^{-1}$ was assumed as the heat of combustion of FAME (Pastore et al., 2013).

The specific energy demand (ED, Eq. (11)) serves as another indicator of the energetic efficiency of the process, in such a way that it can be compared to other values reported in the literature or to other processes. It was calculated using both FAME and bio-crude as mass basis, due to being the products of main interest.

$$ED(\frac{MJ}{kg_{product}}) = \frac{(\sum Q_{step})(1 - r_2)}{m_{product}} \quad (11)$$

3 Results

3.1 Feedstock composition

The properties of sewage sludge (SS) and lipid-extracted sludge (LESS) are outlined in Table 1. Protein was found to be the predominant fraction, accounting for 34.6 wt. % and 38.9 wt.% in sewage sludge and lipid-extracted sludge respectively. which lays within the range available in the literature (30 – 60 wt.%) (Gao et al., 2020), including raw primary sludge , secondary sludge , and digested sludge . The results were quite consistent after 5 runs with 10 parallel repetitions each. Lipids were found to be a minor component of sludge, constituting 13.9 wt.% of the raw material.

Table 1. Characterization of sewage sludge and lipid-extracted sludge.

feedstock	Biochemicals (wt.% daf)[a]				Ash	Elemental content (wt.%)[b]					HHV
	carbohydrates	proteins	lipids	others		C	H	O[c]	N	S	($MJ \cdot kg^{-1}$)
SS	27.9	34.6	13.9	23.6	38.6	25.8	4.6	26.6	3.7	0.7	10.5
LESS	31.3	38.9	-	29.8	45.3	24.0	4.1	22.2	3.8	0.6	10.0

[a:] on the ash-free basis

[b:] on the dry basis

[c:] calculated by difference to the total mass

Elemental analysis was also displayed in Table 1. Special care must be given to the nitrogen content in the feedstock, as this is an important control parameter for the quality of bio-crude , due to the formation of NOx during combustion and demanding treatment during bio-crude upgrading. However, protein-rich sludge may still be desirable because of the higher thermochemical bio-crude conversion efficiencies compared to those obtained with biomass that is richer in more recalcitrant carbohydrates and lignin (Vardon et al., 2012). Raw sludge showed a slightly higher energy content due to its lipids content.

Regarding lipid extraction, many methods with different procedures can be found in publications, of which a summary is provided in Table 2 below. Generally, Soxhlet extraction is quite effective in extracting lipids from both dry and wet sludge (Zhu et al., 2014) (Inoue et al., 1996) (Olkiewicz et al., 2014) (Boocock et al., 1992). It was assumed that all lipids present in the original material were extracted. The organic material was analyzed for carbohydrate, protein and lipid content, others may include lignin and fiber content.

Table 2. Summary of lipid extraction from published sources.

Feedstocks	Fractions	Content wt.%(db)	Methods (solvent)	Reference
Primary mixed waste activated sludge	Crude fat	10.4	-	(Dote et al., 1992)
Digested sludge			ether solvent	(Suzuki et al., 1988)
raw primary sludge	Crude fat	1.9-12.2		
waste active sludge				
Secondary SS	Lipid	8.01		(Wang et al., 2018)
Dewatered SS	Lipid	5.0	Soxhlet extraction	(Inoue et al., 1996)
Liquidized SS	Lipid	10.4	(Diethyl ether)	

Digested sludge	Crude-lipid	<1	Ether solvent	(Vardon et al., 2011)
Dewatered sludge	Lipid	2.5-10.3	Soxhlet extraction (hexane-ethanol)	(Zhu et al., 2014)
		2.2-7.5	Acid hydrolysis	
		3.0-7.5	Water bath shaking	
Primary SS Secondary SS Blended sludge	Lipid	7.7-26.2	Soxhlet extraction (hexane) Liquid-liquid Extraction (hexane)	(Olkiewicz et al., 2014)
Raw sewage sludge	Lipid	12	Soxhlet extraction (chloroform)	(Boocock et al., 1992)
		17-18	Boiling extraction (chloroform)	

-: Not mentioned

3.2 Lipid extraction from sewage sludge

The fatty acid composition of the lipids from the SS was inferred from the results of the FAMEs produced by the *in-situ* transesterification of dry sludge samples. In Figure 1, it can be clearly seen that a significant amount of methyl esters belong to relatively short chains below C18, the cumulative amount of C16:0 and C18:1 was more than 70 %, which was similar to the value in another report (Olkiewicz et al., 2014). The results show a predominance of palmitic acid (C16:0), stearic acid (C18:0), oleic acid (C18:1), in line with previous work. Specifically, palmitic acid was the major saturated fatty acid with a value of 16.4 %, followed by stearic acid accounting for 8.9 %. Oleic acid was the major unsaturated fatty acid, followed by docosahexaenoic acid (C24:1). These fatty acids are exceptionally well-suited for the production of biodiesel (Olkiewicz et al., 2012; Siddiquee and Rohani, 2011; Zhu et al., 2014).

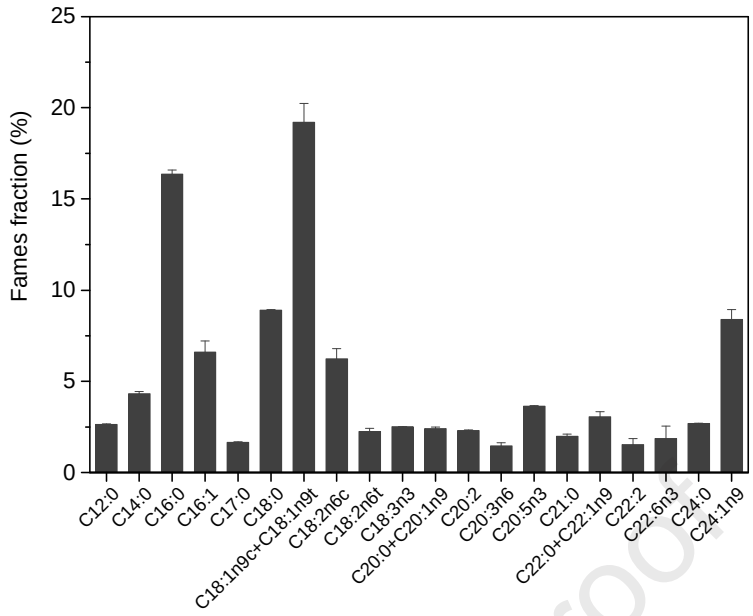


Figure 1. FAMEs analysis of biodiesel obtained from the in-situ transesterification of SS.

3.3 HTL of residue from lipid-extracted sewage sludge (LESS)

In this chapter, raw sewage sludge is used as "reference" to compare the hydrothermal conversion and the products obtained from the HTL of SS and LESS.

3.3.1 HTL conversion

A general comparison between the HTL of SS and LESS is shown in Figure 2, where BC, SR and AQ represent the bio-crude, solid residue and aqueous phases, respectively. Both HTL conversion efficiency (see Eq. (2)) and bio-crude yield increase with the temperature for either feedstock, although HTL of SS shows higher conversions than HTL of LESS for the same operating conditions. Compared to results (average 25 wt.%) reported by other studies using similar operating conditions, the bio-crude yields reported in this manuscript are lower (Liu et al., 2018; Suzuki et al., 1988). At 250 °C and 300 °C, the yields of biocrude obtained from HTL of SS and LESS are basically the same; however, a difference occurs at 350 °C, where

306 the bio-crude yields reach values of 21.3 and 15.4 wt.% for SS and LESS, respectively. In
307 contrast, the SR decreases with the reaction temperature. Compared to HTL of LESS, HTL of
308 SS results in lower solid residue yields at the temperatures used. The AQ forms the dominant
309 part of all the products, between 36.6 to 50.6 wt.% in all cases, and slightly increased with
310 reaction temperature.

311 **3.3.2 Carbon and nitrogen balance**

312 Table 3 shows the elemental balance/distribution in different phases, namely, carbon
313 distribution (CD) and nitrogen distribution (ND), estimated using Eq. (3). For both SS and
314 LESS, the carbon content in the SR significantly decreases from 64.1 to 29.1 % and 58.2 to
315 38.5 % with a temperature increase from 250 to 350 °C, respectively. In the bio-crude phase,
316 the CD correspondingly increases from 13.5 to 34.0 % and from 12.5 to 27.6 %, respectively.
317 The CD of the AQ seems stable, only showing a slight trend of decreasing with the reaction
318 temperature. When considering the gas formed, while the yields are low (< 12 wt.%), the CD
319 shows a rise by a factor of around 4 from 250 to 350 °C.

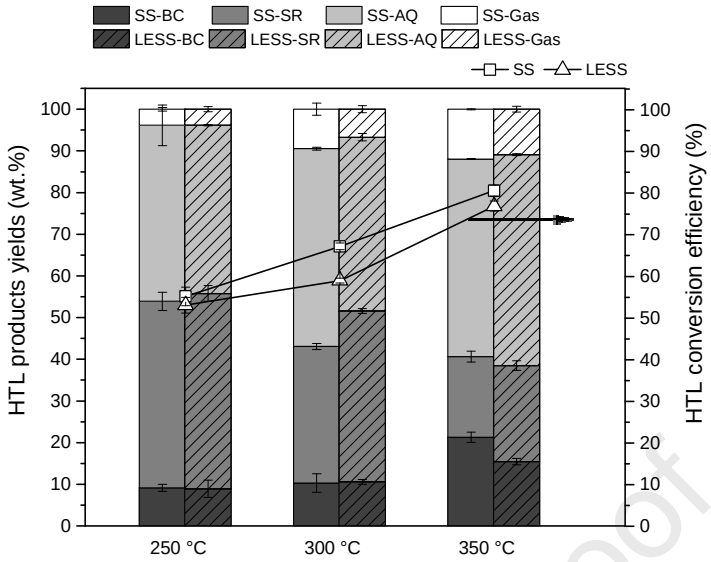


Figure 2. Comparison between HTL of SS and LESS at different temperatures, the yield of the aqueous phase (AQ) was determined as the difference between unity and the sum of the yields of bio-crude (BC), solid residue (SR), and bio-gas (Gas) fractions.

Nitrogen has also been investigated as another important element with regard to the high protein content in both SS and LESS. In contrast to what was discussed for the case of carbon, nearly half the amount of nitrogen is recovered in the aqueous phase under all conditions. Due to this high nitrogen content, the aqueous phase has been considered as a promising medium to cultivate algae, with some success (Biller et al., 2012; Jena et al., 2011). With increasing temperature, the ND in the SR of SS and LESS is significantly reduced from 37.5 to 21.1 % and 35.7 to 22.1 %, respectively. For the case of bio-crude, increasing reaction temperatures seem to lead to increased incorporation of nitrogen, as ND increases from 10.3 to 20.8 % as the temperature rises from 250 to 350 °C, affecting the usability of this phase.

HTL resulted in a considerable proportion of dissolved organic carbon and a major proportion of N in its aqueous phase in every case. Total organic carbon (TOC) analysis was applied to determine water-soluble organic products, as shown in Figure 3 (a). After HTL of SS and of

LESS, TOC contents significantly decreased as the temperature increased from 15500 to 9000 mg/L and 14900 to 6700 mg/L, respectively. While at 250 °C, the TOC in the aqueous phase from SS and LESS are similar, at higher temperatures, the TOC observed for the aqueous phase from LESS were lower than that from SS.

Table 3. Carbon/Nitrogen distribution (CD/ND, wt.%) of various products.

Samples	Bio-crude		Solid		Aqueous phase		Gas	Recovery	
	CD	ND	CD	ND	CD	ND	CD	CD	ND
SS-250 °C	13.5	10.3	64.1	45.5	19.6	48.8	2.5	99.8	104.6
SS-300 °C	17.1	12.1	53.6	38.0	15.6	47.1	6.2	92.6	97.2
SS-350 °C	34.0	20.8	29.1	25.6	14.8	42.2	8.2	86.2	88.7
LESS-250 °C	12.5	11.0	54.6	40.2	21.3	42.2	2.2	90.7	93.4
LESS-300 °C	17.3	11.5	49.2	35.9	15.6	45.2	4.6	86.7	92.6
LESS-350 °C	27.6	16.7	38.5	31.3	14.0	44.6	9.4	89.6	92.5

Regarding ammonium (NH_4^+), seen in Figure 3 (b), the opposite trend was observed. After HTL of SS and LESS, NH_4^+ concentrations steadily increased with the temperature from 4000 to 6000 mg/L and 3000 to 5000 mg/L, respectively. In addition, the NH_4^+ content present in the AQ phase after HTL of SS was higher than that of LESS under the same conditions.

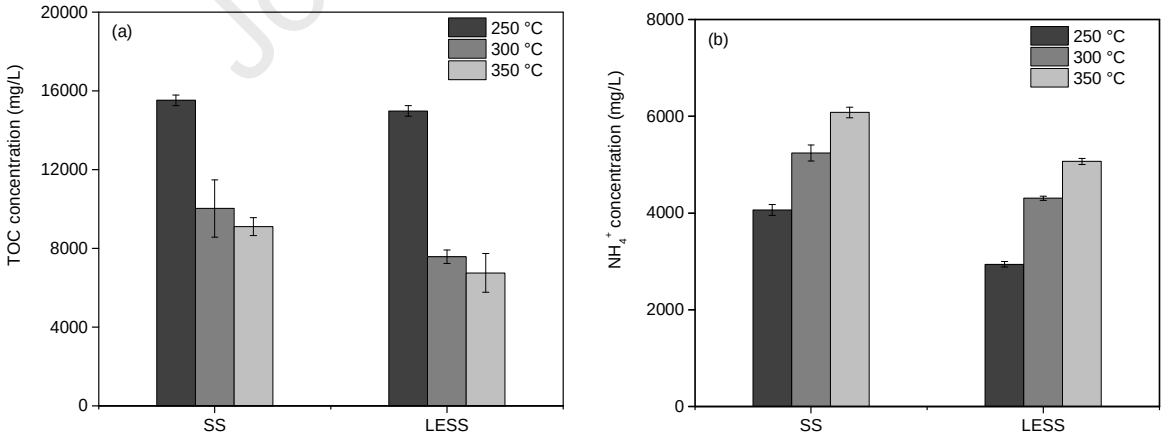


Figure 3.Total organic carbon concentration (a) and ammonium concentration (b) in the aqueous phase from HTL of SS and LESS

3.3.3 Energy content of the products

Table 4 summarizes element ratios and HHV for all bio-crude and solid products. Further

detailed elemental analyses are shown in Table S1. The extracted lipids exhibit HHV very similar to that of FAME (39.29 vs 39.5 $MJ \cdot kg^{-1}$) (Pastore et al., 2013).

When comparing the raw SS and LESS, the bio-crude obtainedfrom HTL shows a lowering in the H/C and O/C ratios and higher HHV. The effect of temperature is most noticeable when comparing the results at 250 °C and 300 °C, but the change between 300 °C and 350 °C is subtle and may lay within experimental uncertainty; this trend can be observed for experiments using both SS and LESS. Regarding the solid residue, HTL treatment led to lower H/C and O/C ratios when compared to the feedstocks. The effect of temperature seems to be similar to that found for bio-crude. All heating values ranged from 28 to 40 $MJ \cdot kg^{-1}$, close to those reported for bio-crude produced from sewage sludge (35 – 40 $MJ \cdot kg^{-1}$) (Qian et al., 2017) and paper sludge (35 – 37 $MJ \cdot kg^{-1}$) (Xu and Lancaster, 2008), but lower than that of petroleum crude oil (43 $MJ \cdot kg^{-1}$) (Speight, 2015). Low N/C ratios in the bio-crude and high values in the solid residue confirm the results presented in Table 3.

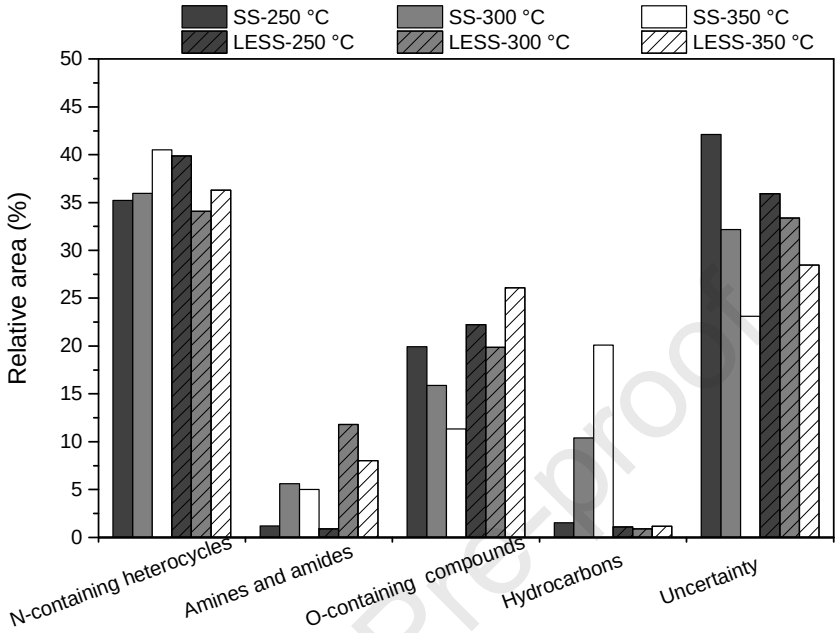
Table 4. Elemental composition (atomic ratio), higher heating value ($MJ \cdot kg^{-1}$) of bio-crude and solid residue.

HTL	Bio-crude				Solid residue			
	H/C	O/C	N/C	HHV	H/C	O/C	N/C	HHV
Raw SS					0.77	2.14	0.12	10.54
LESS					0.70	2.07	0.13	10.03
Extracted lipids	1.86	0.11	0.01	39.29				
SS-250 °C	0.18	1.62	0.09	32.29	0.38	1.56	0.09	10.02
SS-300 °C	0.13	1.57	0.09	34.60	0.16	1.41	0.09	10.35
SS-350 °C	0.09	1.57	0.07	37.26	0.22	1.39	0.11	6.40
LESS-250 °C	0.24	1.56	0.12	28.85	0.48	1.52	0.10	8.29
LESS-300 °C	0.11	1.45	0.09	34.76	0.49	1.31	0.10	7.11
LESS-350 °C	0.12	1.45	0.08	34.91	0.27	1.33	0.11	6.82

362 **3.3.4 Bio-crude composition**

363 Figure 4shows the groups of chemicals in the bio-crudes obtained. The identification of
364 organic compounds was achieved by comparing the spectra of sample components (limited to
365 the top 50 compounds based on the peak-normalized volume) with those in the electronic
366 library of NIST. The organic components were analyzed using the area normalization
367 method (Li et al., 2014). Detailed categories of constituents can be seen in Table S2 in the
368 Supporting Information. The identified components account for more than 56 % and 64 % of
369 the total species in the bio-crude derived from SS and LESS, respectively. The major detected
370 compounds are N-containing heterocycles such as pyrazines, pyrrolidinones, and indoles,
371 similar species have been described in a previous report (Zhai et al., 2014). These fractions
372 slightly increase with reaction temperature in the case of HTL of SS. A decrease is observed
373 from HTL of LESS. O-containing compounds form the second largest constituent of bio-crude,
374 mainly composed of phenolic compounds. It is observed that O-containing compounds in the
375 bio-crude from HTL of SS greatly decrease with increasing temperature, whereas, conversely,
376 a higher amount of O-containing compounds are formed in the case of HTL of LESS. The
377 yield of hydrocarbons seems to be very influenced by the temperature (an increase from 1.5 to
378 20.1 %) for the case of SS, but an almost absence of these compounds in bio-crude produced
379 from LESS, due to negligible lipid content.
380 Regarding amines and amides, the lowest fractions are produced at 250 °C which may be a
381 temperature too low to promote this type of reaction. Bio-crude from LESS shows a higher
382 value of said components, mostly including piperidines and acetamides. While, around 1.5 %

383 hexadecanamide could be found in bio-crude stemming from HTL of SS at 300 °C, indicating
384 reactions between lipid and protein contents.



385
386 Figure 4. Chemical groups represented inbio-crude obtained from HTL of SS and LESS under
387 different temperatures.

388 TGA analysis was applied to study the three stages of weight loss and its relationship to the
389 results of GC-MS analyses of the composition of the bio-crude. The TGA curves of the 6
390 kinds of bio-crude from HTL of SS and LESS are shown in Fig. S1 in the Supporting
391 Information. All HTL bio-crudes show the same TGA curve progression, with a similar
392 decomposition process. However, the derivative thermogravimetry (DTG) plot seems to be
393 quite different. The DTG curves of bio-crude from HTL of SS at 300 and 350 °C show weight
394 loss at 100 °C, indicating the presence of water. A relatively significant weight loss takes
395 place between 180 °C and 380 °C with a peak at 290 °C. Regarding the HTL of LESS, a
396 relatively significant weight loss occurs between 150 °C and 330 °C with no specific peak.
397 Another significant decomposition process is triggered at around 430 °C.

Table 5 further provides boiling point distributions which were calculated based on the weight loss during TGA measurement. Small differences in boiling point distribution trends are observed for HTL bio-oils derived from SS and LESS. The most significant fractions correspond to compounds of volatilities similar to those of kerosene or diesel oil (200 °C to 400 °C), in agreement with results found by Liu et al. (Liu et al., 2018). LESS bio-crude contains more fractions in the gasoline range (110 – 200 °C) and less in the heavy diesel (300 – 400 °C) when compared to SS bio-crude. The amount of distilled fractions between 200 °C and 550 °C, which can generally be used in petroleum refineries (Huang et al., 2016), accounted for around 71 to 74.1 wt.% in bio-crude from HTL of SS, and 67.2 to 70.9 wt.% in bio-crude from HTL of LESS. Accordingly, it is worth noting that the heavy crude fraction (> 550 °C) in all bio-crude is larger than 25.9 wt.%, the value reported from Liu et al. (Liu et al., 2018), limiting the chances of direct refinery integration and requiring costly upgrading. More residues at higher boiling points (> 800 °C) were obtained in the crude derived from HTL of LESS.

Table 5. Boiling point distribution of bio-crude from HTL of SS and LESS.

Distillation Range (°C)	typical application[a]	Distribution (wt.%) in Bio-crude					
		SS			LESS		
		250 °C	300°C	350 °C	250 °C	300 °C	350°C
20-110	Bottle gas	3.3	2.6	2.8	2.3	3.8	1.6
110-200	Gasoline	12.7	11.8	13	14.7	19.7	14.7
200-300	Jet fuel/Light diesel	24.9	22.9	23.8	23.2	21.3	24.0
300-400	Heavy diesel	22	20.4	14.4	13.2	12.3	12.6
400-550	Vacuum Gas Oil	11.2	15.6	17	15.2	13.8	14.3
<550		*74.1*	*73.3*	*71*	*68.5*	*70.9*	*67.2*
550-700	Heavy Fuel Oil	3.9	2.8	5.1	3.7	6.9	4
700-800	Asphalt	1.7	1.3	3.1	2.4	5.2	2.0

>800	Residue	20.3	22.6	20.8	25.4	17	26.8

[a]: Handbook of Petroleum Product Analysis (Speight, 2015)

4 Discussion

4.1 Possible reaction pathways for HTL of LESS

Figure 2 shows that the conversion of SS and LESS via HTL is comparable, suggesting that the residue after lipid extraction can be considered a suitable feedstock for the HTL process. For both cases, increasing temperature leads to increased conversion, along with a decrease of organic content in the solid residue. A lower amount of solid residue overall is found when using raw SS, indicating that the lipids in the SS converted into water-soluble compounds, such as organic acids, a fact supported by the comparatively higher TOC concentration observed in the aqueous phase produced from SS (Figure 3 (a)).

For lower temperatures (250 °C), bio-crude seems to be most likely produced by reactions between carbohydrates and proteins, such as Maillard reactions. In the case of LESS, the higher protein content may compensate for the absence of lipids in the feedstock. It is confirmed that Maillard reactions play a significant role in bio-crude production, which is supported by the N-containing heterocycles detected by GC-MS (Fan et al., 2018; Zhang et al., 2016). However, when the temperature increases to 350 °C, a larger amount of bio-crude is produced from HTL of SS. This can be explained as follows: In one way, polar or water-soluble fatty acids in the aqueous phase further convert or condense into crude-like products. Fatty acids could undergo decarboxylation to produce alkenes or alkanes (Watanabe et al., 2006), indicated by the significantly higher amounts of hydrocarbons found in the crude phase, as shown in Figure 4. In another way, these fatty acids get converted into bio-crude

constituents by cross-linking reactions, like amide formation with proteins.

However, a fact to be taken into consideration is the limited solubility of lipids in DCM, which hinders their recovery and influences the estimated values of conversion. This may explain the similar yields of bio-crude reported for SS and LESS at 250 °C (Figure 2). It has been reported that soap formation can happen at low temperatures in the base reaction medium, which hinders product separation during the extraction of lipids from sewage (Mondala et al., 2009). When the temperature increases to 350 °C, more bio-crude from HTL of SS is found, which could partly be from DCM-extracted lipids.

HTL of palmitic acid

HTL of palmitic acid (PA) at three different temperatures was conducted to support the above-made hypotheses. PA was selected as model fatty acid as it has been widely confirmed as the major fatty acid in sewage sludge (Olkiewicz et al., 2014; Olkiewicz et al., 2012; Tang et al., 2019; Zhu et al., 2014), also identified from FAME as shown in Figure 1. Despite the increase in temperature, the carbon distribution to the solid residue was kept practically constant when increasing temperature from 250 to 300 °C. Analysis of the solid residue from HTL of PA (Table S3 in the Supporting Information) showed that this fraction is essentially indistinguishable from palmitic acid. This fact stems from low solubility of this lipid in DCM, affecting the estimation of the conversion, which presents low values when compared to HTL of SS or LESS (6.4 % at 250 °C, to 10.9 % at 350 °C, Figure 5). Accordingly, the TOC concentration in the aqueous phase is low, increasing from 64 to 259 mg/L, suggesting that PA is resistant to decomposition below 350 °C. This is in agreement with the findings from HTL

of LESS and SS, where lipids only slightly contribute to the bio-crude at lower temperatures. The main portion of the unreacted PA remains solid and is collected as “solid residue”, a part of the PA is extracted by a DCM solvent to form bio-crude products. This outcome is likely due to the limited amount of DCM being unable to fully dissolve all of the fatty acids, suggesting the bio-crude yield depends on the amount of solvent and the separation procedure. This observation is greatly consistent with the reports from Watson et al.(Watson et al., 2018) and Qian et al. (Qian et al., 2017), that the extraction solvent selection should be carefully considered and normalized for the reporting of hydrothermal liquefaction yields and energy efficiency values.

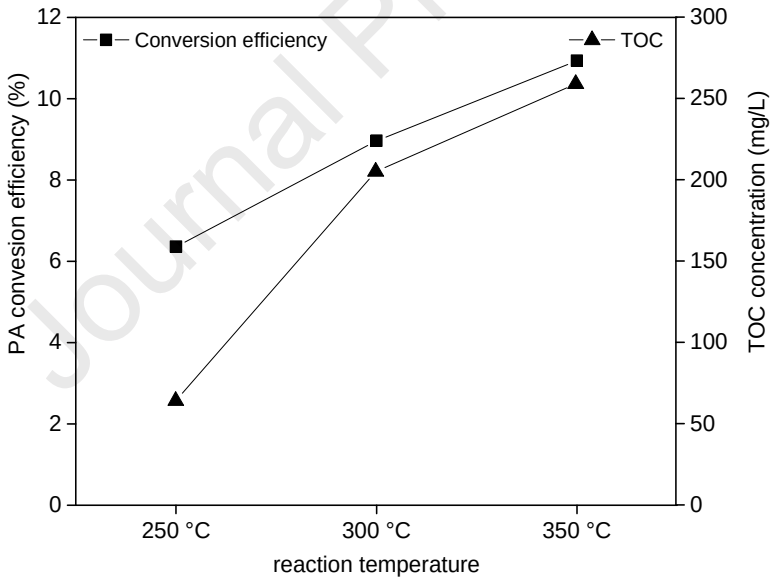
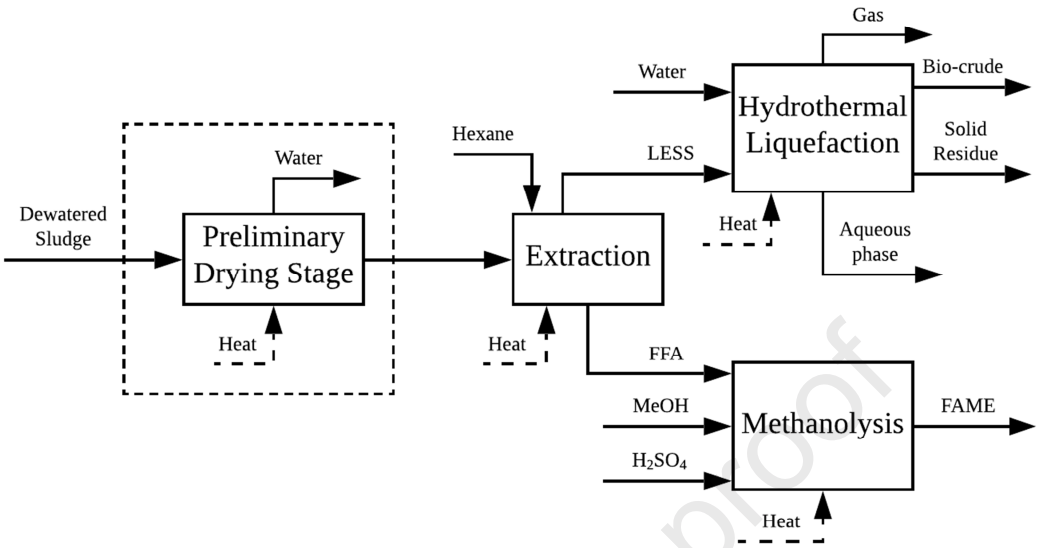


Figure 5. Evolution of conversion and TOC concentration in the aqueous phase for HTL of PA (palmitic acid) at different temperatures.

4.2 Integration of lipid extraction and HTL of LESS

Figure 6 presents a block flow diagram of the processes considered in this work. The mass yields of the liquid fuels (bio-crude and extracted lipid) obtained in the different process

468 configurations of are shown in Table 6.



469

470 Figure 6. Block flow diagram of combined lipid extraction, HTL and methanolysis for FAME
471 production. The checkered box represents a part of the process that may be disregarded due to
472 direct lipid extraction from wet sludge.

473 The combined yields represent the total yield of extracted lipids and bio-crude produced from
474 LESS. Accordingly, the HHV is calculated from that of both components. When looking at
475 the evolution of the bio-crude yield without considering lipid extraction, the jump in yield is
476 significant between 300 °C and 350 °C, while being negligible between 250 °C and 300 °C. A
477 similar, albeit more moderate effect can be found when performing HTL of LESS. The yield
478 of extracted lipid exceeds the yield in bio-crude at 250 °C and 300 °C, leading to combined
479 yields (HTL+extraction) which are more than double the value obtained using HTL alone. At
480 350 °C, the high bio-crude yields diminish the effect of this coupling. Moreover, the
481 calculated HHV is higher than those of the bio-crude from HTL of SS. It appears that the

482 greater efficiency of value-added fuel can be obtained from combining these two methods.
483 Since lipids are commonly seen as biodiesel feedstock, which contains fewer heteroatoms in
484 the target products, it is possible and efficient to extract lipids before conducting the HTL
485 conversion in order to achieve a better energy valorization.

Table 6. Comparing the Mass yields of lipid extraction and HTL and their combination. Values in brackets correspond to the HHV of the product ($MJ \cdot kg^{-1}$).

Temperature (°C)	Extraction yield (wt.%)	Liquid fuel products yields (wt.%)		
		Bio-crude of SS	Bio-crude of LESS	Combined Lipid extraction plus bio-crude
250	13.9 (39.4)	9.13 (32.29)	8.86 (28.85)	22.76 (35.29)
300		10.27 (34.60)	10.55 (34.76)	24.45 (37.39)
350		21.26 (37.26)	15.39 (34.91)	29.29 (37.04)

486 However, the higher nitrogen content in the bio-crude from HTL of LESS has to be kept in
487 mind, as it does not meet fuel standards. Post-treatments like upgrading and distillation could
488 be applied as effective, albeit costly, processes to reduce or remove nitrogen from bio-crude
489 (Elliott et al., 2013; Ramirez et al., 2015). For the latter case, lesser efforts must be taken to
490 reduce the acidity of the distillates owing to the extraction of fatty acids.

Table 7. Energy requirements ($MJ \cdot kg^{-1}$) for different steps of the integrated process(without considering heat recovery).

	Combined process	HTL	Drying	Extraction	Methanolysis	Total
With drying	LESS-250 °C	45.1	112.8	61.0	2.2	221.1
	LESS-300 °C	54.9				230.9
	LESS-350 °C	64.7				240.7
Without drying	LESS-250 °C	45.1	-	61.0	2.2	108.3
	LESS-300 °C	54.9				118.1
	LESS-350 °C	64.7				127.9

491 Table 7shows the heat requirements for the combined process. Drying is a substantial part of
492 the energy demand, contributing to around half of the heat demand when employed. HTL and

493 lipid extraction show very similar heat demands, while the energy demand of methanolysis is
494 seemingly negligible.
495 In Table 8, estimations of energy recovery (ER, Eq. (5)), energy consumption ratio (ECR, Eq.
496 (6)) and energy demand (ED) per mass of produced bio-crude/FAME are shown. The
497 estimation has been carried out based on two cases, A and B, which employ different
498 efficiencies for combustion and heat recovery, respectively. ECR is estimated for different
499 scenarios, considering the production of only bio-crude (ECR_{BC}), both bio-crude and bio-char
500 (ECR_{BC+SR}), the former plus extracted lipid ($ECR_{BC+SR+L}$), and lipids converted into FAME
501 ($ECR_{BC+SR+FAME}$). While conventional lipid extraction requires the drying of sludge (Dufreche
502 et al., 2007; Pastore et al., 2013), recently the feasibility of performing extraction of non-dried
503 sludge (Olkiewicz et al., 2014; Pastore et al., 2013) has been shown, thus the estimations on
504 energy efficiency considers the process with and without drying step.
505 . Since the effect of temperature on the HHV of the formed phases can be neglected, the
506 energy recovery is mostly determined by the product distribution, favoring higher
507 temperatures for bio-crude formation. SS shows lower energy recovery when compared to
508 those found for LESS at the same temperature, due to the absence of the lipid phase, which
509 features a high HHV. Also, ECR values are given in Table 8. Employing only HTL in case A
510 assuming conservative efficiencies, the calculated ECR for SS is higher than 1 at temperatures
511 below 350 °C, suggesting that HTL is energetically inefficient, which aligns with the findings
512 from Xu et al.(Xu and Lancaster, 2008). However, the energy efficiency can be improved with
513 more favorable conditions, as shown for case B, and energy breakeven can always be

514 achieved. Table 8also shows that ECR obtained for SS is lower than that obtained for LESS at
515 the same temperature, due to the energy demand for extraction and drying processes (Table 7).
516 A similar trend was reported by Vardon et al. (Vardon et al., 2012), where ECR obtained from
517 algae was lower than that from defatted algae. However, in their work, a favorable energy
518 balance was achieved (ECR 0.44 – 0.55), probably owing to the high bio-crude yields
519 (36 – 45 wt.%) and the exclusion of energy consumption for drying and lipid extraction.
520 The combined process (HTL+extraction) present higher ECRs and energy demands than the
521 case where only HTL is considered, also explainable by the additional heat requirements for
522 drying and extraction. The minimal effect of methanolysis, aided by the slightly higher HHV
523 of FAME, leads to a negligible difference in ECR between the lipid case and the FAME case
524 for all temperatures. The omission of the drying step leads to a halving of the energy demand
525 of the process. The values of the energy demand for the process with drying reported in this
526 work are lower than those obtained by Pastore et al. (Pastore et al., 2013) for the methanolysis
527 of dewatered sludge (140 – 187 $MJ \cdot kg^{-1}_{FAME}$). However, when disregarding drying, the
528 process reaches values compared to the combined process presented by Pastore et al.
529 (44 – 60 $MJ \cdot kg^{-1}_{FAME}$) (Pastore et al., 2013). When including the energy demand for drying,
530 this value increases greatly.

531

Table 8. Estimation of the Energy Recovery (ER) and Energy Consumption Ratio (ECR), as well as the Energy Demand (ED) of HTL and combined processes. Value assuming a FAME yield of 8.5 wt.% of the dry sludge.

	Process	ER	ECR $_{BC}$		ECR $_{BC+SR}$		ECR $_{BC+SR+L}$		ECR $_{BC+SR+FAME}$		Energy demand MJ/(kg BC)		Energy demand MJ/(kg FAME)	
		(%)	A	B	A	B	A	B	A	B	A	B	A	B
Only HTL	SS-250 °C	85.4	1.52	0.95	0.31	0.19	-	-	-	-	34.4	27.5	-	-
	SS-300 °C	82.1	1.54	0.96	0.78	0.48	-	-	-	-	37.2	29.7	-	-
	SS-350 °C	78.2	0.81	0.50	0.70	0.44	-	-	-	-	21.2	16.9	-	-
With drying	LESS-250 °C	98.3	1.91	1.19	0.76	0.47	1.91	1.19	1.93	1.20	185.4	147.6	110.5	88.4
	LESS-300 °C	92.3	1.69*	1.05*	0.94*	0.59*	2.02	1.26	2.03	1.26	169.7	135.1	115.4	92.4
	LESS-350 °C	96.7	1.37*	0.85*	1.06*	0.66*	2.05	1.28	2.07	1.28	121.9	97.1	120.3	96.3
Without drying	LESS-250 °C	98.3	1.91*	1.19*	0.76*	0.47*	0.93	0.58	0.94	0.59	88.9	70.4	54.1	43.3
	LESS-300 °C	92.3	1.69*	1.05*	0.94*	0.59*	1.02	0.64	1.04	0.65	85.2	67.5	59.0	47.2
	LESS-350 °C	96.7	1.37*	0.85*	1.06*	0.66*	1.08	0.67	1.10	0.68	63.7	50.5	63.9	51.1

*: only HTL of LESS is considered.

Conclusion

This work focuses on a novel proposal to maximize energy valorization of sewage sludge, by integrating lipid extraction and hydrothermal liquefaction of the lipid-extracted sewage sludge residue. The extracted lipid can be employed for the production of biodiesel (FAME), while the remaining organics in the residual sewage sludge (lipid-extracted, LESS) can be further converted into value-added products via hydrothermal liquefaction. The combined approach improves the liquid bio-fuel products (29.29 wt.%) compared with HTL of un-extracted sludge (21.26 wt.%) at optimized temperature. Possible key reactions during HTL have been proposed based on additional experiments with model substance. The majority of lipids in the sewage sludge cannot be converted into bio-crude at lower temperatures. Maillard reactions significantly contribute to the formation of bio-crude components but show high nitrogen contents. Regarding the energetic efficiency of the process, energy recovery of around 98 % could be achieved by the coupled process, which has a significant temperature dependency. Analysis of the energy consumption ratio (ECR, 1.91 – 2.05) of the process disfavors the coupled process due to the energetic requirements of drying (112.8 $MJ \cdot kg^{-1}$) and lipid extraction (61.0 $MJ \cdot kg^{-1}$). However, the energetic efficiency can be improved if making use of state-of-the-art technology.

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Highlights

- Raw sewage sludge was submitted to lipid extraction.
- Raw and lipid-extracted sewage sludge, and a model lipid were subjected to HTL.
- Combined process (HTL+extraction) yielded 29.3 wt.% liquid fuel-like products.
- Combined process showed an energy recovery up to 98 % based on HHV comparison.
- Energy consumption ratio shows a significant temperature dependency.

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.