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Reduction of inorganics from macroalgae *Laminaria digitata* and spent mushroom
 compost (SMC) by acid leaching and selective hydrothermal liquefaction.

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- 12

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Abstract: Hydrothermal liquefaction (HTL) is a promising route for producing bio-crude from 13 various biomass feedstocks. However, high content of inorganic constituents in biomass like 14 macroalgae Laminaria Digitata and Spent Mushroom Compost (SMC) affect the conversion 15 process and the resulting fuel products. This research studied the effects of different acid 16 leaching treatments on such feedstocks, subsequent HTL and bio-crude properties. Leaching 17 18 treatments were performed using five different agents: deionised water, acetic acid, citric acid, 19 sulfuric acid, and hydrochloric acid. Performance of leaching was evaluated by analyzing both leached biomass and HTL products by elemental analysis, ash content, inductively coupled 20 21 plasma (ICP) analysis, and X-ray diffraction (XRD) analysis. Catalytic and non-catalytic HTL of 22 both feedstocks before and after treatment were performed in 10mL micro reactor at 400°C with holding time of 15 min and pressures (27-30 MPa). For macroalgae, sulfuric acid and 23 24 hydrochloric acid were found the most effective in reducing the ash content from 30.42% to 20.45% and 20.87%, respectively, followed by acetic and citric acid treatment that could reduce 25 the ash content to 21.5% and 22.15% respectively. Similarly for SMC, citric acid and acetic 26 acid were found the most effective in reducing the ash content from 50.34% to 37.04% and 27 39.94% respectively. Citric acid did not show significant leaching of organic components such 28 as carbohydrates and proteins, and represented a less toxic and hazardous option for the 29 30 leaching. The results from HTL of untreated and citric acid treated biomass showed that the acid leaching resulted in an increase in bio-crude yields from 20.7 to 29.2 % (dry ash-free basis) 31 for macroalgae and from 22.9 to 25.1 % for SMC. 32

33 Keywords: Hydrothermal liquefaction; inorganic constituents; ash content; acid leaching; bio-

34 crude.

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37 **1 Introduction**

Depletion of fossil fuel resources and environmental issues associated with greenhouse gases 38 (GHG) are the main reasons increasing the attention towards renewable energy resources like 39 biomass. Various thermochemical technologies can be utilized to convert the biomass into 40 biofuels [1]. Among them, hydrothermal liquefaction (HTL) has received increasing interest in 41 the past decades as a process for converting biomass into drop-in biofuels and chemicals [2-3]. 42 Higher temperatures and pressures to maintain the water as a liquid are generally employed [4]. 43 The biomass feedstock can be processed directly, without an energy-consuming drying step, 44 since water acts both as solvent and catalyst [5-6]. High reactivity and superior ionic product 45 (Kw) of supercritical water break down biomass complex polymers including carbohydrates, 46 lipids, and proteins into smaller molecules that can be converted into bio-crude, water soluble 47 48 chemicals, solid residue, and gas [4, 7] depending on the catalysts, solvents, feedstock composition, and pretreatment methods employed [8-10]. 49

50 To avoid negative impacts caused by food production, novel non-food biofuel feedstocks need to be identified and utilised. One option is to utilise marine biomass, notably fast-growing, large 51 52 marine plants such as macroalgal kelps. Brown macroalgae, L. Digitata is considered as the potential biomass source for energy production due to their relatively fast growth rates, ease of 53 harvesting, and low pre-production cost [11]. One of the studies reported the use of L. Digitata 54 biomass to generate bio-crude via HTL. They reported a bio-crude yield of 17.6 wt% (daf) basis 55 with a higher heating value (HHV) of 32 MJ/kg [12]. Another study on HTL of brown algae 56 Saccharina ssp. reported a yield of 8.7 and 27.7% of bio-crude depending on the harvesting 57 times and conditions of the macroalgae [13]. Spent Mushroom Compost (SMC) is commonly 58 used as a low cost commercial and private scale fertilizer. Approximately 5 kg of SMC is 59 generated from each 1 kg of grown button mushrooms on the farm [14]. That led to ca. 17 60 million metric tonnes of the byproduct in 2007 globally. In Europe alone, SMC availability is 61 estimated to be 47 million tonnes per year, which results in a potential of ~130 000 tonnes of 62 available feedstock per day [15]. 63

Although HTL has the potential to generate high yields of bio-crude, there are some limitations that need to be addressed if L. digitata and SMC to be used as feedstocks. One of the major

limitations is their high ash content (L. Digitata up to 30% and SMC up to 50%). The high ash 66 content is due to the presence of inorganic constituents, mostly alkali and alkaline earth metallic 67 species (AAEMs). This reduces the yield and quality of the generated bio-crude and restricts 68 their alternative usage in direct combustion and gasification processes [9, 16]. Also, 69 physicochemical characteristics of bio-crude can be changed easily during storage due to the 70 presence of higher AAEMs content in the bio-crude, because the AAEMs catalyze the 71 polymerization reactions and thereby increase the viscosity [17]. High ash content can bring 72 additional challenges to the catalytic refining of bio-crude such as decrease in catalyst activities, 73 74 poisoning, and coking [9, 16]. It is reported that AAEMs present in feedstocks inactivated the catalysts used in the downstream upgrading processes of bio-crude [17-18]. 75

Leaching has been suggested by many authors to be an efficient, fast and low cost way to significantly reduce the ash content of a biomass material [19-21]. Therefore many leaching experiments using different agents such as deionized water [22-23], acetic acid [17, 24], hydrochloric acid [25-26], sulphuric acid [27-28], and citric acid [18] had been conducted.

80 Post-leaching, water washing steps are carried out in order to remove residual acids. It is well known that alkaline HTL media lead to lower amounts of produced char. Meanwhile, HTL of 81 82 acidic feedstock slurries ends up generating higher amounts of solid residues. This is believed to be brought on by the fact that low pH media promote dehydration, resulting in the production 83 of easily polymerising unsaturated compounds. HTL of model cellulose shows that acidic 84 conditions lead to lower yields exactly due to the polymerisation of 5-furfural [29]. 85 Neutralisation step via water washing is a welcome alternative especially when strong acids 86 (e.g. hydrochloric acid and sulphuric acid) are used in order to remove chlorine and sulphates 87 which enhance equipment corrosion and fouling in biocrude production and refining, 88 respectively. 89

In this study, we investigate the impacts of different leaching treatments on both macroalgae *L. Digitata* and SMC biomass. Five different treatments were selected for the study: two strong acids (hydrochloric acid and sulfuric acid), two weak acids (citric and acetic acid), and deionised water. The study focused on analysis of the biomass changes in its physical–chemical composition, and the impact of the pretreatment on the bio-crude yield through the HTL process. The pre-treated and non-treated biomass samples were analyzed and compared for their metal content and organic composition.

98 2 Materials and Methods

99 2.1 Raw materials

Macroalgae *L. Digitata* and Spent Mushroom Compost (SMC) biomass were selected for this
study. The former was collected from Easdale Island, Scotland and the latter was received from
a local Danish mushroom farm (St. Restrup Champignon). The samples were pre-dried at 105
°C for 24 h, pulverized and stored at room temperature for analysis. The particle size fraction of
200µm was used for the experiments.

105

106 2.2 Leaching process

L. Digitata and SMC were leached with five different agents for reduction of inorganics: 107 deionised water, acetic acid, citric acid, hydrochloric acid and sulphuric acid, and all acid 108 agents were purchased from Sigma Aldrich, which are in analytical grade of 99.9%. The acids 109 were diluted to 1.0 wt% solutions. In a typical leaching treatment, 10.0 g of biomass were 110 soaked in 100mL of 1.0% acid solution under magnetical stirring (1000 rpm) at 30 °C for 4 h. 111 Lower acid concentration (1.0%) was selected because of lower water consumption for removal 112 of residual acid during post leaching process. After acid leaching, the biomass residues were 113 subjected to water washing in order to eliminate residual acids. The washing was carried out in 114 several steps, each of which consisted of mixing the leached biomass with 200 ml of deionised 115 water, stirring the mixture well and separating the two phases gravimetrically after 116 117 centrifugation. Treated biomass samples were dried in an electric oven at 105 °C for 24 h, and 118 then stored prior to be used for analyzing. Leaching treatments and analysis were done in triplicate and mean values are reported. 119

120

121 **2.3 Biomass characterization methods**

122 **2.3.1** *Proximate and ultimate analysis*

Thermogravimetric analysis (TGA) of treated and untreated biomass samples was applied on Simultaneous Thermal Analyzer (STA) 6000 (PerkinElmer) for determination of moisture, ash, volatile and fixed carbon contents. All samples were heated from 50 to 950 °C at a rate of 10 °C/min under nitrogen atmosphere. Ultimate analysis was carried out by using a vario MACRO cube (Elementar). All the measurements were conducted three times and the mean values are reported.

130 2.3.2 Inductively coupled plasma- optical emission spectroscopy (ICP-OES)

The alkali and alkaline earth metallic species (AAEMs) of each biomass sample were 131 quantified using inductively coupled plasma-optical emission spectroscopy (ICP-OES) 132 following Microwave Assisted Acid Digestion. The samples were prepared for analysis 133 according to USEPA SW-846 Method 3051A - Microwave Assisted Acid Digestion of Solids 134 135 and Oils (US. EPA, 2007). The microwave digestion system was an Anton Paar Multiwave 3000 equipped with high-pressure fluoropolymer lined ceramic digestion vessels. The digest of 136 each sample was subsequently diluted to 50.0 mL using type 1 ultra-pure water (PURELAB 137 Ultra, Elga LabWater, Glostrup, Denmark). 138

139 The ICP-OES was a Thermo iCap 6300 duo ICP-OES equipped with a Cetac ASX-260 autosampler. The spectrometer was operated in radial view mode with a RF power of 1.15 kW. 140 The plasma and auxiliary gas flows were 12 L min⁻¹ and 1.0 L min⁻¹, respectively. The sample 141 introduction system was a Cetac U5000AT+ ultrasonic nebulizer. The nebulization gas pressure 142 was 0.2 MPa and the sample uptake rate was 2 mL min⁻¹. The ICP-OES was calibrated using 143 matrix matched multi-element external standards (PlasmaCAL, SCP Science, Quebec, Canada). 144 Three standards and one blank were used for calibration of each element using three emission 145 lines. Yttrium was used as internal standard. All standards were traceable to National Institute 146 147 of Standards and Technology (NIST).

148

149 2.3.3 X-ray diffraction analysis

Pretreated and untreated samples of L. Digitata and SMC were analyzed by X-ray diffraction (XRD) analysis on an Empyrean (PANalytical, Netherlands) system under Cu K α radiation (λ =0.1542 nm; 45kV and 40 mA) in a 2 θ range between 5° and 70° at a step size of 0.013°. The measurements were conducted three times and the mean values are reported.

154

155 2.4 Hydrothermal liquefaction methodology

Hydrothermal liquefaction experiments were carried out in a 10 mL stainless steel tubular micro batch reactor at 400 °C and 25-30 MPa with a holding time of 15 minutes. Biomass slurry was prepared with a composition of 85% deionized water, 15% dry biomass, and 5% K₂CO₃ of total biomass (in case of a catalytic run) by weight. In a typical experiment, homogenized biomass slurry (~5 g) was loaded in the reactor and sealed. The system was purged twice to pressures of ~8 Mpa, flushed and finally pressurized to 2±0.1 MPa. The reactor was heated in a preheated fludized sand bath (Techne SBL-2D). At the end of the reaction, the reactor was quenched in a cold water bath. Gas products were vented in fume hood. HTL products were separated into bio-crude fraction, water soluble fraction and solid residues according to the procedure schematically shown in Figure 1.

The water phase was poured out of the reactor and filtered using pre-weighed Whatman No. 5 filter paper to collect the solid product. The reactor was washed using acetone (Sigma Aldrich) to recover the biocrude. The acetone and bio-crude mixture was filtered and evaporated using a rotary evaporator to remove the acetone. The solid residue was oven-dried at 105 °C for 24 h. All HTL experiments were performed in triplicates.



195 2.5 Analysis of HTL bio-crude

Bio-crude yield was calculated separately on an ash-and-moisture free basis using the following
equation (wt.%) [30]:

(1)

198

Where, $Y_{\text{bio-crude}}$ is the bio-crude yield (wt%) on a dry weight basis, W_{biocrude} is the mass of biocrude (g), $W_{\text{feedstock}}$ is the mass of the biomass used in the reactor, W_{moisture} and W_{ash} are the moisture and ash content of the feedstock, respectively. The HHVs of the generated bio-crude were calculated by Channiwala and Parikh formula [31].

$$HHV(MJ/kg) = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211Ash$$
 (2)

 $Y_{bio-crude}(wt.\%) = \frac{W_{biocrude}}{\left(W_{feedstock} - W_{moisture} - W_{ash}\right)} \times 100\%$

206

207 **3 Results and Discussions**

208 **3.1** Chemical analyses of the samples

The effectiveness of the different biomass leaching treatments was evaluated considering the impact of the treatments on the ash contents of the biomass. The ultimate and proximate analysis results of untreated and treated samples were shown in Table 1.

Treatment	Ash	Total Moisture	VM	FC ^a	HHV ^b
	(wt%)	(wt%)	(wt%)	(wt%)	(MJ/kg)
L.digitata					
Untreated	30.42	2.88	49.59	17.11	6.96
Deionized water	28.58	2.1	48.34	20.98	6.60
Acetic acid	21.5	3.91	64.3	10.29	13.93
Hydrochloric acid	20.87	2.46	69.16	7.51	15.83
Sulfuric acid	20.45	2.9	68.47	8.18	14.88
Citric acid	22.15	3.71	64.15	9.99	14.56
Citric acid (5%)	5.96	1.3	75.74	16.99	N/A
SMC					
Untreated	50.34	2.87	36.89	9.9	5.92
Deionized water	47.19	2.89	40.90	9.02	7.34
Acetic acid	39.94	3.27	47.20	9.59	8.93
Hydrochloric acid	41.21	3.38	48.16	7.25	7.53
Sulfuric acid	44.40	2.71	43.75	9.14	6.40
Citric acid	37.04	2.59	49.99	10.38	9.60
Citric acid (5%)	16.66	1.57	67.69	14.06	N/A

Table 1 | Proximate analysis of treated and untreated biomasses.

²¹³ ^aFixed Carbon obtained by difference between 100% and the sum of ash, moisture, and

volatile matter.

²¹⁵ ^bCalculated by Channiwala and Parikh formula [31]

As shown in Table 1, comparing to the untreated L. Digitata sample, the ash content of the 216 deionized water leaching sample decreased from 30.42% in the untreated biomass to 28.58% 217 only, and the ash content of acid leaching samples decreased significantly to 20.45% and even 218 5.96%, when a 5% citric acid solution was employed. In case of SMC, the ash content of the 219 deionized water leaching sample slightly decreased from 50.34% in the untreated biomass to 220 221 47.19%, and the ash content of acid leaching samples decreased to 37.04% and 16.66% with 1% and 5% citric acid solutions, respectively. The ash content of samples decreased remarkably 222 and volatile content increased dramatically after leaching process, which indicates leaching 223 process could improve biomass fuel properties such as heating value. Despite showing similar 224 leaching efficiencies in L. Digitata and SMC as 1% solution (27.2% and 26.4%), citric acid 225 performed better in macroalgae when used as a 5% leaching agent (80.4% ash reduction 226 compared to 66.9% in SMC). The fivefold increase in acid concentration led to 3 and 2.5 times 227 higher leaching efficiencies in the two biomass feedstocks, respectively. 228

As mentioned above, after water leaching, the ash content of L. Digitata decreased from 229 30.42% to 28.58%, hence ~6% are water-soluble ash components. After 1% acid leaching, the 230 ash content of samples decreased to 20.45–22.15%, here the ~27–33% of the lost matter consist 231 232 of both water-soluble and acid-soluble portions. Similarly, the ash content of SMC decreased from 50.34% to 47.19%, hence ~6% are water-soluble. Whereas after 1% acid solution 233 leaching, the ash content of samples decreased to 37.04-44.40%, here the ~12-26% of the lost 234 235 mass is composed of both water- and acid-soluble fractions. Considering the ~6% of watersoluble part, the minerals present in the two feedstocks comprise of a significant amount of 236 water-soluble components (mainly in the form of chlorides, nitrates, carbonates and 237 phosphates) [32-33]. The experiments with 5% citric acid solutions, however, showed that 238 stronger acid leaching removes more acid-solubles. Namely, in L. Digitata, water-solubles 239 added up to just 7.5% of the total removed ash, while in SMC, the same was true for 9.4% of 240 the removed ash. This confirms the previously described higher efficiency of acid leaching. 241

The organic components of biomass are composed of different hydrocarbons which mainly consist of C and H atoms. The molecular mass of C is much higher than H, thus the C/H wt% ratio reflects variances in amounts of hydrocarbons. When some hydrocarbons are washed away, the C/H wt% ratio decreases. As shown in Table 2, the C/H wt% ratio of raw and treated samples fluctuates between 7.19 and 7.55 in case of L. Digitata, and 7.77 and 9.31 for SMC. The C/H wt% ratio decreased slightly after the leaching processes, which illustrates that a fraction of organic components were removed from samples during the leaching process.

The contents of AAEMs in untreated and treated samples are listed in Table 3. K and Na contents of untreated L. Digitata are higher than other metal contents and this is common in brown macroalgae. After distilled water leaching, very small amount of AAEMs were removed, which suggests that the majority of these AAEMs were present in the form of water-insoluble salts. Comparing to water leaching, the amount of AAEMs had different degrees of decline after acid leaching, and such decline was related with acidity of leaching agents. Especially after leaching by strong acids such as HCl and H2SO4, more than 90% AAEMs were removed, and, comparing to their reduction by water leaching, it can therefore be deduced that most of AAEMs were present in the form of water-insoluble salts.

 Table 2 | Ultimate analysis of treated and untreated biomasses.

Treatment	C (%)	H (%)	N (%)	S (%)	O (%) ^c	C/H ratio
L.digitata						
Untreated	28.23	3.73	2.31	0.98	34.56	7.55
Deionised water	27.23	3.72	2.58	1.06	36.86	7.30
Citric acid	39.66	5.40	3.37	0.83	28.42	7.33
Acetic acid	38.58	5.26	2.63	0.71	30.90	7.32
Hydrochloric acid	40.86	5.63	2.58	0.96	27.74	7.25
Sulfuric acid	38.90	5.40	2.56	0.76	30.28	7.19
SMC						
Untreated	29.14	3.12	1.95	0.48	15.44	9.31
Deionised water	30.20	3.27	1.86	0.31	15.93	9.22
Citric acid	33.09	4.25	2.34	0.45	22.81	7.77
Acetic acid	31.59	4.26	2.32	0.71	21.16	7.39
Hydrochloric acid	29.62	3.88	2.26	0.79	22.23	7.63
Sulfuric acid	28.78	3.41	2.03	0.48	20.88	8.42

^c Obtained by difference between 100% and the wt% of C, H, N, S, and ash.

Treatment	K	Na	Ca	Mg
L.digitata				
Untreated	92.74	41.74	15.35	9.73
Deionised water	89.81	37.66	17.33	8.57
Citric acid	16.76	6.23	19.72	6.34
Acetic acid	16.64	6.70	21.29	8.62
Hydrochloric acid	4.57	1.54	5.08	1.41
Sulfuric acid	3.66	1.25	4.56	1.08
SMC				
Untreated	18.72	2.22	69.03	3.97
Deionised water	0.8	0.14	67.33	2.87
Citric acid	0.61	0.09	44.13	1.59
Acetic acid	0.63	0.11	42.08	1.68
Hydrochloric acid	0.66	0.10	19.58	1.17
Sulfuric acid	0.60	0.06	34.26	1.28

Table 3 | Alkali and alkaline earth metallic species (AAEMs) of treated and untreated

biomasses (mg/g, by dry weight).

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Ca and K content of untreated SMC is higher than other metal content, while this is not surprising because of excess agricultural fertilization with common gypsum and potash fertilizer during cultivation of mushroom compost. After distilled water leaching, K and Na were almost completely removed comparing to Ca and Mg, which suggests that the majority of K and Na were present in the form of water-soluble salts. After leaching by strong acid such as as HCl and H₂SO₄, more than 50 % of Ca and Mg were removed depending upon the acidity of the agents. It means most of Ca and Mg were present in the form of water-insoluble salts.

Acid especially strong acid leaching is more effective on removal of AAEMs, but it might introduce a negative impact on physicochemical structure of the samples. Thus as a complementary means of investigation, XRD was used to follow the change of crystalline structures as the leaching agents varied.

290

291 **3.2** Crystalline structure of treated and untreated biomass

Figure 2 shows changes in the X-ray diffraction pattern of untreated and treated biomass samples.

The diffraction pattern of untreated *L. Digitata* in Figure 2 (a) showed eight peaks of different intensity between 25° and 70° at different 2θ . On diffractograms of the samples after treating with different agents, almost all the peaks disappeared except in case of deionised water

treatment. These results indicated that all the acidic treatments have converted the L. Digitata into complete amorphous phases.

In case of SMC, the diffraction pattern of untreated SMC Figure 2 (b) showed numerous peaks

- of different intensity between 20° and 70° at 20. Almost all the peaks on diffractograms of the
- samples remained same even after treating with different solvents. So leaching treatments had

no impacts on crystallization of the SMC samples.





342 3.3 Hydrothermal liquefaction of untreated and treated biomass

Although strong acids HCl and H₂SO₄ were better pretreatment agents for leaching both L. 343 Digitata and SMC, it could be associated with negative impact on physicochemical structure of 344 the biomass led to the loss of biochemical composition of the biomass. The yield of biocrude in 345 HTL depends on the amount of biochemicals such as carbohydrates, proteins, and lipids present 346 in the biomass. The strong acids were not selected due to their toxicity and also it is very high 347 working load to neutralise the biomass during post-leaching water washing step after the use of 348 349 strong acids like HCl and H₂SO₄. Although citric acid treatment did not show the highest leaching potential, it was selected for further HTL studies due to its more experimental friendly 350 nature and lower water requirements after post-leaching to neutralise both L.digitata and SMC. 351

Proximate analysis of the untreated and treated biomasses (treated with citric acid) was performed and resulted in higher fixed carbon percentage and lower ash content than the untreated one. Also, the citric acid treated biomass had a higher content of volatiles than the untreated biomasses.

356

357 3.3.1 HTL products yields

HTL products and yields of citric acid treated and untreated biomasses are presented in Table4&5.

359 4**&**5.

Table 4 | HTL Products obtained from treated and untreated biomasses.

361

	Bio-crude	Solid residue	Aqueous	Gas phase
	(g)	(g)	phase (g)	(g)
L.digitata				
Untreated (non-Cat.)	0.08	0.27	4.29	0.35
Untreated (Cat.)	0.10	0.31	4.15	0.43
Treated with Citric (Cat.)	0.16	0.14	4.33	0.35
SMC				
Untreated (non-Cat.)	0.08	0.44	3.99	0.48
Untreated (Cat.)	0.07	0.42	3.96	0.54
Treated with Citric (non-Cat.)	0.11	0.41	4.25	0.23

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371	Table 5	HTL Products	yields and	ash content	obtained f	from treated	and untreated
			-				

372 biomasses.

373

	Bio-6	crude	Solid resi	due	Ash (wt %)
	Yield ^d (wt%)	St. dev.	Yield ^d (wt%)	St. dev.	
L.digitata					
Untreated (non-Cat.)	16.15	1.73	37.40	0.86	0.12
Untreated (Cat.)	20.69	5.31	42.03	0.99	0.75
Treated with Citric (Cat.)	29.15	2.23	19.89	1.49	0.45
SMC					
Untreated (non-Cat.)	22.86	6.18	58.99	2.95	3.56
Untreated (Cat.)	20.42	7.74	57.42	4.61	0.60
Treated with Citric (non-Cat.)	25.06	0.29	55.14	2.56	4.04

³⁷⁴ ^dDry ash-free (DAF) basis

375

As anticipated from the proximate analysis, a higher bio-crude yield (29.15%) was obtained 376 from the catalytic HTL of citric acid treated L. Digitata than that of untreated through catalytic 377 HTL, which had a bio-crude yield of 20.69%. Similarly in case of SMC, a higher bio-crude 378 yield (25.06%) was obtained from the non-catalytic HTL of citric acid treated SMC than that of 379 untreated SMC through non-catalytic HTL i.e. 22.86%. There are no significant differences in 380 381 elemental carbon and hydrogen composition in bio-crude samples obtained from both untreated and treated biomasses (Table 6). High oxygen and nitrogen content in bio-crude suggests that 382 an upgrading step is required after the HTL process to convert the product into a drop-in fuel. 383 384

385

5 **Table 6** | Ultimate analysis of biocrude obtained from treated and untreated biomasses.

386

	C (%)	H (%)	N (%)	S (%)	O (%) ^e
L.digitata					
Untreated (non-Cat.)	76.93	8.57	4.96	0.57	8.83
Untreated (Cat.)	76.04	7.63	4.08	0.60	10.89
Treated with Citric (Cat.)	76.40	8.07	3.92	0.62	10.53
SMC					
Untreated (non-Cat.)	76.39	7.62	3.82	1.01	7.59
Untreated (Cat.)	74.92	7.91	3.17	0.97	12.43
Treated with Citric (non-Cat.)	64.41	7.62	2.77	0.90	20.24

^e Obtained by difference between 100% and the wt% of C, H, N, S and ash.

388

In summary for the HTL primary fuel target, the bio-crude, we observe an increase in yield and

390 lower ash content, along with decrease in solid residues after the leaching pretreatment.

Although assessing process economics is not among the main objectives of this study, it is 391 necessary to discuss the issues of additional costs and resources associated with feedstock 392 leaching inclusion. Due to low acid concentrations necessary for efficient removal of 393 inorganics, the additional amount of water required for the proposed pre-treatment step is the 394 key factor. The economics of acid leaching are highly dependent on local water availability, 395 water costs and expenses related to process water treatment. Furthermore, costs encountered 396 due to HTL system plugging and fouling are production site specific, namely due to the varying 397 system design and the implemented char evacuation technologies. In the end, case studies shall 398 be carried out to weigh the economic advantages and disadvantages of acid leaching 399 400 pretreatment for continuous HTL plants.

As far as the results from this study go, the inclusion of feedstock acid leaching is seen as a 401 HTL enabling strategy. The fact that experiments with macroalgae and SMC at batch scale 402 exhibited signs of potential blockage problems (i.e. major agglomeration of solids in the 403 reactor) raise concern for the viability of continuous HTL with such feedstocks. On the other 404 hand, biomass leaching did not lead to decreased bio-crude yields and quality. Given that cheap 405 biomass often has a low calorific value, is of high humidity and exhibits a high content of 406 407 inorganics, system blockages are the major obstacle for large scale continuous HTL processing. 408 Waste biomass valorisation via HTL is known for its high energetic efficiency [34] and the capacity to produce high quality biofuel precursors. The possibility of successfully converting 409 410 low-cost high-ash sustainable feedstocks might as well lead to enabling acid leaching as an 411 additional pretreatment step.

412

413 **3.4 Water demand for biomass neutralisation**

414 Water demand was quantified for each leaching procedure with the two studied feedstocks. In 415 the case of L. digitata, the acetic and citric acid leached biomass reached neutral pH after 6 washing steps, whereas algae exposed to hydrochloric and sulphuric acid leaching remained at 416 pH 5 and 4, respectively, even after 8 washing steps. Acetic, citric and sulphuric acid leached 417 SMC reached neutral pH already after 3 washing steps, whereas hydrochloric acid pretreated 418 419 biomass remained at pH 5 after 8 consecutive washing steps. Here, 3, 6 and 8 washing steps signify process water consumption levels of 0.06, 0.12 and 0.16 L for each gram of initial 420 421 feedstock.

Water washing as a post acid leaching neutralisation technique inherently increases process 422 water demands hence future facilities must take this and the raised subsequent waste water 423 treatment requirements into account when carrying out techno-economic analyses of continuous 424 HTL processing. HTL specific research is needed on the alternative chemical neutralisation 425 route. Acid neutralisation via the addition of bases is a straightforward reaction chemically, 426 however the acidic and basic compounds present in the feedstock might have adverse effects on 427 the production of biocrude due to precipitation, especially in terms of potentially impaired 428 yields and promoted formation of solids. Arguably, when comparing water and chemical 429 neutralisation, the effect of superior organic matter preservation might counteract the possible 430 drop in biocrude yields caused by acid driven recondensation reactions. 431

432

433 4 Conclusions

The effects of leaching pretreatments using five different leaching agents (deionised water, 434 acetic acid, citric acid, sulfuric acid, and hydrochloric acid) on HTL of L. Digitata and SMC 435 biomass were studied. It was found that all the leaching pretreatments decreased the inorganic 436 contents in the biomasses as expected. While, citric acid was selected as the best leaching agent 437 438 because it was able to remove maximum AAEMs without using a large amount of water in the 439 post leaching process to neutralize the biomasses. In addition, it represents a more eco-friendly alternative. The results of HTL of both treated and untreated L. Digitata and SMC showed that 440 441 the leaching treatment resulted in an increase in bio-crude yield from 20.7 to 29.2 % (dry ashfree basis) for macroalgae and from 22.9 and 25.1 % for SMC. 442

443

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