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

3  
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6  
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12  
13 **Abstract:** Hydrothermal liquefaction (HTL) is a promising route for producing bio-crude from  
14 various biomass feedstocks. However, high content of inorganic constituents in biomass like  
15 macroalgae *Laminaria Digitata* and Spent Mushroom Compost (SMC) affect the conversion  
16 process and the resulting fuel products. This research studied the effects of different acid  
17 leaching treatments on such feedstocks, subsequent HTL and bio-crude properties. Leaching  
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  
20 leached biomass and HTL products by elemental analysis, ash content, inductively coupled  
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  
23 with holding time of 15 min and pressures (27-30 MPa). For macroalgae, sulfuric acid and  
24 hydrochloric acid were found the most effective in reducing the ash content from 30.42% to  
25 20.45% and 20.87%, respectively, followed by acetic and citric acid treatment that could reduce  
26 the ash content to 21.5% and 22.15% respectively. Similarly for SMC, citric acid and acetic  
27 acid were found the most effective in reducing the ash content from 50.34% to 37.04% and  
28 39.94% respectively. Citric acid did not show significant leaching of organic components such  
29 as carbohydrates and proteins, and represented a less toxic and hazardous option for the  
30 leaching. The results from HTL of untreated and citric acid treated biomass showed that the  
31 acid leaching resulted in an increase in bio-crude yields from 20.7 to 29.2 % (dry ash-free basis)  
32 for macroalgae and from 22.9 to 25.1 % for SMC.

33 **Keywords:** Hydrothermal liquefaction; inorganic constituents; ash content; acid leaching; bio-  
34 crude.

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## 37 **1 Introduction**

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

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

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

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

76 Leaching has been suggested by many authors to be an efficient, fast and low cost way to  
77 significantly reduce the ash content of a biomass material [19-21]. Therefore many leaching  
78 experiments using different agents such as deionized water [22-23], acetic acid [17, 24],  
79 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  
81 known that alkaline HTL media lead to lower amounts of produced char. Meanwhile, HTL of  
82 acidic feedstock slurries ends up generating higher amounts of solid residues. This is believed  
83 to be brought on by the fact that low pH media promote dehydration, resulting in the production  
84 of easily polymerising unsaturated compounds. HTL of model cellulose shows that acidic  
85 conditions lead to lower yields exactly due to the polymerisation of 5-furfural [29].

86 Neutralisation step via water washing is a welcome alternative especially when strong acids  
87 (e.g. hydrochloric acid and sulphuric acid) are used in order to remove chlorine and sulphates  
88 which enhance equipment corrosion and fouling in biocrude production and refining,  
89 respectively.

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

97

## 98 **2 Materials and Methods**

### 99 **2.1 Raw materials**

100 Macroalgae *L. Digitata* and Spent Mushroom Compost (SMC) biomass were selected for this  
101 study. The former was collected from Easdale Island, Scotland and the latter was received from  
102 a local Danish mushroom farm (St. Restrup Champignon). The samples were pre-dried at 105  
103 °C for 24 h, pulverized and stored at room temperature for analysis. The particle size fraction of  
104 200µm was used for the experiments.

105

### 106 **2.2 Leaching process**

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

120

### 121 **2.3 Biomass characterization methods**

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

123 Thermogravimetric analysis (TGA) of treated and untreated biomass samples was applied on  
124 Simultaneous Thermal Analyzer (STA) 6000 (PerkinElmer) for determination of moisture, ash,  
125 volatile and fixed carbon contents. All samples were heated from 50 to 950 °C at a rate of 10  
126 °C/min under nitrogen atmosphere. Ultimate analysis was carried out by using a vario MACRO  
127 cube (Elementar). All the measurements were conducted three times and the mean values are  
128 reported.

129

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

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

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

148

### 149 **2.3.3 X-ray diffraction analysis**

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

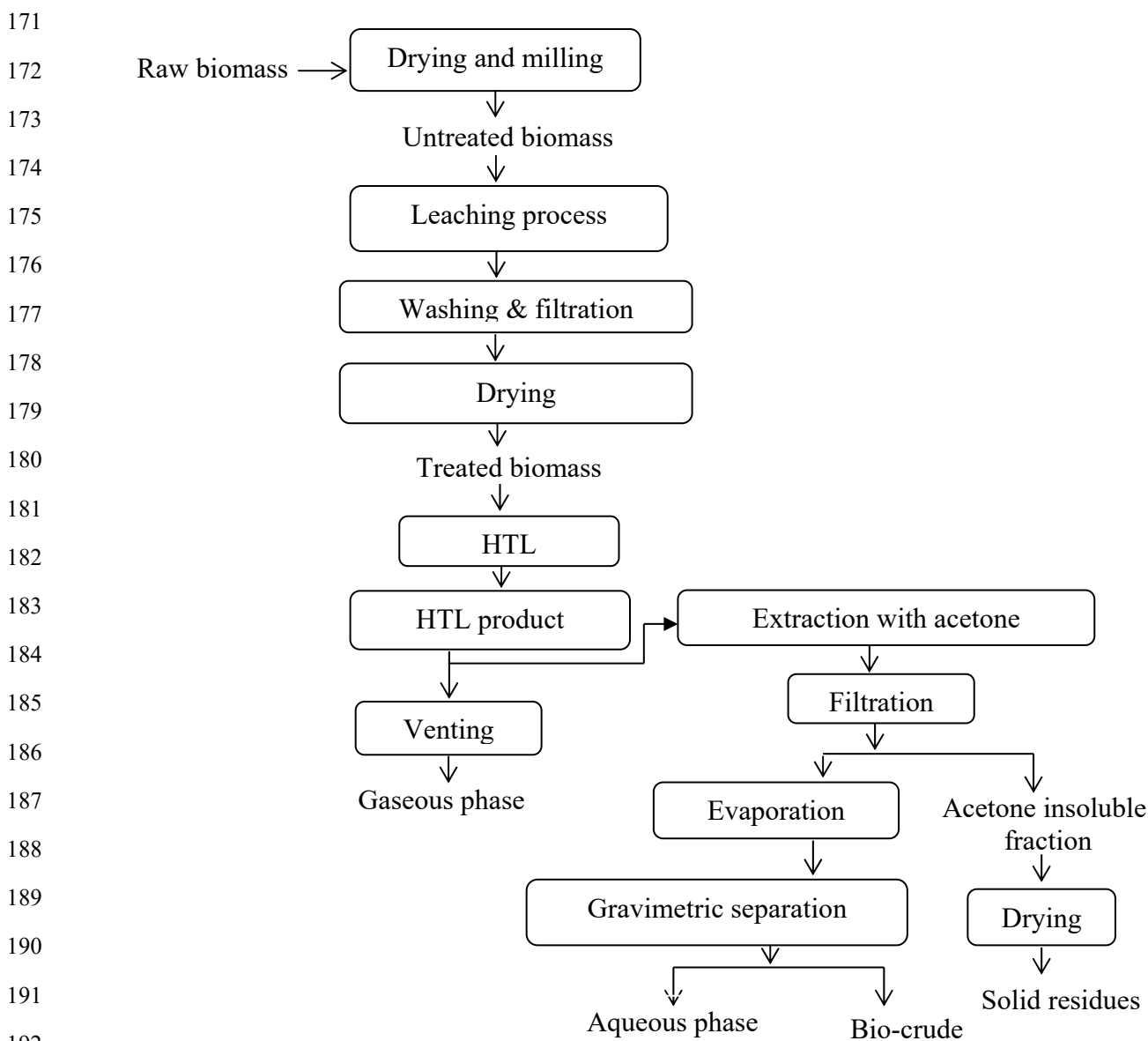
154

### 155 **2.4 Hydrothermal liquefaction methodology**

156 Hydrothermal liquefaction experiments were carried out in a 10 mL stainless steel tubular  
157 micro batch reactor at 400 °C and 25-30 MPa with a holding time of 15 minutes. Biomass slurry  
158 was prepared with a composition of 85% deionized water, 15% dry biomass, and 5% K<sub>2</sub>CO<sub>3</sub> of  
159 total biomass (in case of a catalytic run) by weight. In a typical experiment, homogenized  
160 biomass slurry (~5 g) was loaded in the reactor and sealed. The system was purged twice to  
161 pressures of ~8 Mpa, flushed and finally pressurized to 2±0.1 MPa. The reactor was heated in a

162 preheated fluidized sand bath (Techne SBL-2D). At the end of the reaction, the reactor was  
163 quenched in a cold water bath. Gas products were vented in fume hood. HTL products were  
164 separated into bio-crude fraction, water soluble fraction and solid residues according to the  
165 procedure schematically shown in Figure 1.

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



193 **Figure 1.** Experimental procedure for biomass leaching and HTL operations.  
194

195 **2.5 Analysis of HTL bio-crude**

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

198 
$$Y_{bio-crude} (wt.\%) = \frac{W_{biocrude}}{(W_{feedstock} - W_{moisture} - W_{ash})} \times 100\% \quad (1)$$

199  
200

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

205 
$$HHV(MJ / kg) = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211Ash \quad (2)$$

206

207 **3 Results and Discussions**

208 **3.1 Chemical analyses of the samples**

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

212 **Table 1** | Proximate analysis of treated and untreated biomasses.

| Treatment                | Ash (wt%) | Total Moisture (wt%) | VM (wt%) | FC <sup>a</sup> (wt%) | HHV <sup>b</sup> (MJ/kg) |
|--------------------------|-----------|----------------------|----------|-----------------------|--------------------------|
| <b><i>L.digitata</i></b> |           |                      |          |                       |                          |
| 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                      |
| <b><i>SMC</i></b>        |           |                      |          |                       |                          |
| 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                      |

213 <sup>a</sup>Fixed Carbon obtained by difference between 100% and the sum of ash, moisture, and  
 214 volatile matter.

215 <sup>b</sup>Calculated by Channiwala and Parikh formula [31]



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

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

242 The organic components of biomass are composed of different hydrocarbons which mainly  
243 consist of C and H atoms. The molecular mass of C is much higher than H, thus the C/H wt%  
244 ratio reflects variances in amounts of hydrocarbons. When some hydrocarbons are washed  
245 away, the C/H wt% ratio decreases. As shown in Table 2, the C/H wt% ratio of raw and treated  
246 samples fluctuates between 7.19 and 7.55 in case of *L. Digitata*, and 7.77 and 9.31 for SMC.

247 The C/H wt% ratio decreased slightly after the leaching processes, which illustrates that a  
 248 fraction of organic components were removed from samples during the leaching process.  
 249 The contents of AAEMs in untreated and treated samples are listed in Table 3. K and Na  
 250 contents of untreated *L. Digitata* are higher than other metal contents and this is common in  
 251 brown macroalgae. After distilled water leaching, very small amount of AAEMs were removed,  
 252 which suggests that the majority of these AAEMs were present in the form of water-insoluble  
 253 salts. Comparing to water leaching, the amount of AAEMs had different degrees of decline  
 254 after acid leaching, and such decline was related with acidity of leaching agents. Especially  
 255 after leaching by strong acids such as HCl and H<sub>2</sub>SO<sub>4</sub>, more than 90% AAEMs were removed,  
 256 and, comparing to their reduction by water leaching, it can therefore be deduced that most of  
 257 AAEMs were present in the form of water-insoluble salts.

258

259 **Table 2** | Ultimate analysis of treated and untreated biomasses.

260

| Treatment                 | C (%) | H (%) | N (%) | S (%) | O (%) <sup>c</sup> | C/H ratio |
|---------------------------|-------|-------|-------|-------|--------------------|-----------|
| <b><i>L. digitata</i></b> |       |       |       |       |                    |           |
| 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      |
| <b><i>SMC</i></b>         |       |       |       |       |                    |           |
| 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      |

261 <sup>c</sup> Obtained by difference between 100% and the wt% of C, H, N, S, and ash.

262

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273

274 **Table 3** | Alkali and alkaline earth metallic species (AAEMs) of treated and untreated  
 275 biomasses (mg/g, by dry weight).  
 276

| Treatment                 | K     | Na    | Ca    | Mg   |
|---------------------------|-------|-------|-------|------|
| <b><i>L. digitata</i></b> |       |       |       |      |
| 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 |
| <b><i>SMC</i></b>         |       |       |       |      |
| 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 |

277  
 278  
 279 Ca and K content of untreated SMC is higher than other metal content, while this is not  
 280 surprising because of excess agricultural fertilization with common gypsum and potash  
 281 fertilizer during cultivation of mushroom compost. After distilled water leaching, K and Na  
 282 were almost completely removed comparing to Ca and Mg, which suggests that the majority of  
 283 K and Na were present in the form of water-soluble salts. After leaching by strong acid such as  
 284 as HCl and H<sub>2</sub>SO<sub>4</sub>, more than 50 % of Ca and Mg were removed depending upon the acidity of  
 285 the agents. It means most of Ca and Mg were present in the form of water-insoluble salts.  
 286 Acid especially strong acid leaching is more effective on removal of AAEMs, but it might  
 287 introduce a negative impact on physicochemical structure of the samples. Thus as a  
 288 complementary means of investigation, XRD was used to follow the change of crystalline  
 289 structures as the leaching agents varied.

290

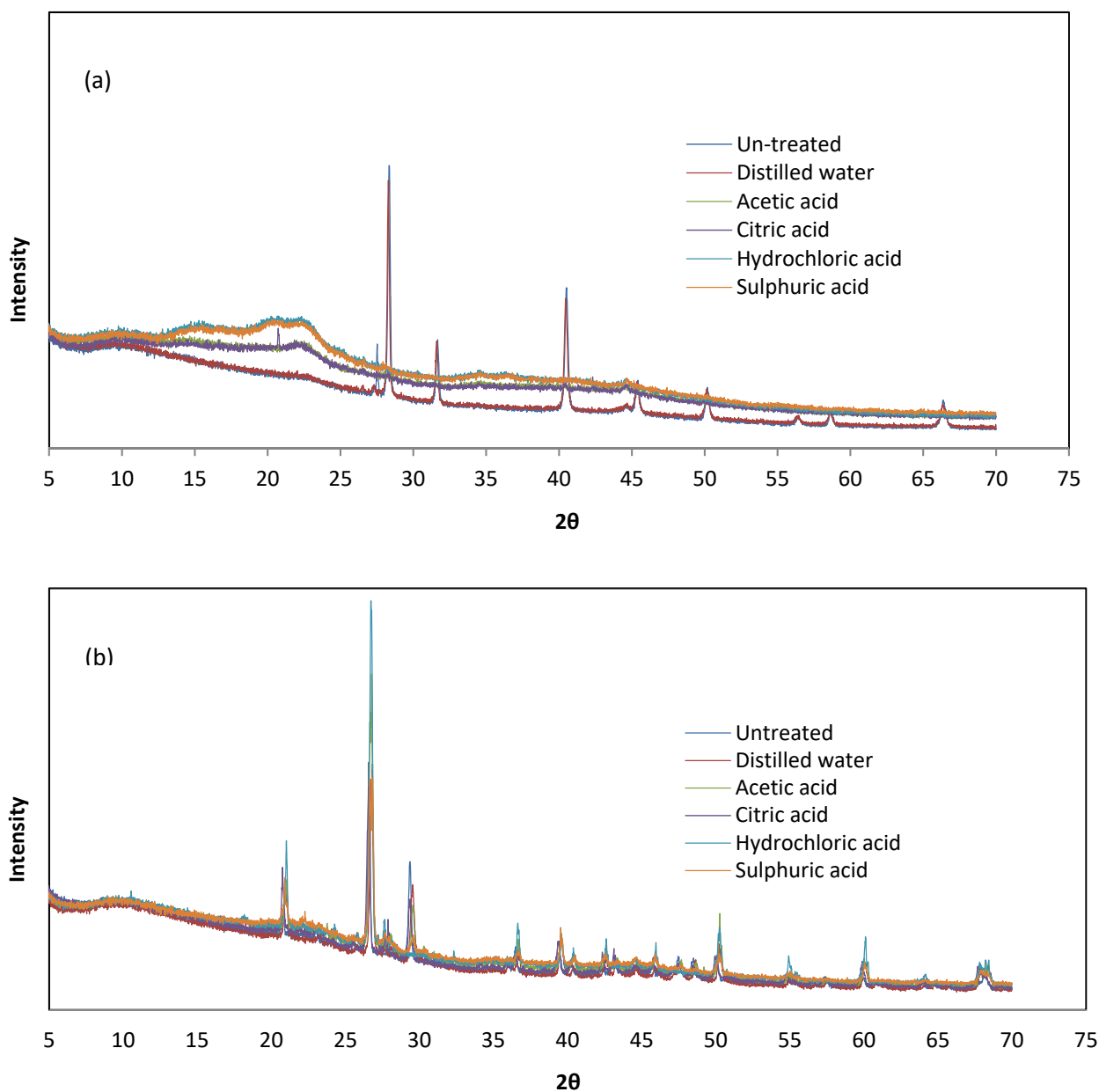
### 291 **3.2 Crystalline structure of treated and untreated biomass**

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

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

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

299 In case of SMC, the diffraction pattern of untreated SMC Figure 2 (b) showed numerous peaks  
300 of different intensity between 20° and 70° at 2θ. Almost all the peaks on diffractograms of the  
301 samples remained same even after treating with different solvents. So leaching treatments had  
302 no impacts on crystallization of the SMC samples.



340 **Figure 2.** XRD patterns of treated and untreated biomass. (a) *L. Digitata* and (b) SMC.

341

342 **3.3 Hydrothermal liquefaction of untreated and treated biomass**

343 Although strong acids HCl and H<sub>2</sub>SO<sub>4</sub> were better pretreatment agents for leaching both *L.*  
344 *Digitata* and SMC, it could be associated with negative impact on physicochemical structure of  
345 the biomass led to the loss of biochemical composition of the biomass. The yield of biocrude in  
346 HTL depends on the amount of biochemicals such as carbohydrates, proteins, and lipids present  
347 in the biomass. The strong acids were not selected due to their toxicity and also it is very high  
348 working load to neutralise the biomass during post-leaching water washing step after the use of  
349 strong acids like HCl and H<sub>2</sub>SO<sub>4</sub>. Although citric acid treatment did not show the highest  
350 leaching potential, it was selected for further HTL studies due to its more experimental friendly  
351 nature and lower water requirements after post-leaching to neutralise both *L. digitata* and SMC.  
352 Proximate analysis of the untreated and treated biomasses (treated with citric acid) was  
353 performed and resulted in higher fixed carbon percentage and lower ash content than the  
354 untreated one. Also, the citric acid treated biomass had a higher content of volatiles than the  
355 untreated biomasses.

356

357 **3.3.1 HTL products yields**

358 HTL products and yields of citric acid treated and untreated biomasses are presented in Table  
359 4&5.

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

361

|                                | <b>Bio-crude<br/>(g)</b> | <b>Solid residue<br/>(g)</b> | <b>Aqueous<br/>phase (g)</b> | <b>Gas phase<br/>(g)</b> |
|--------------------------------|--------------------------|------------------------------|------------------------------|--------------------------|
| <b><i>L. digitata</i></b>      |                          |                              |                              |                          |
| 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                     |
| <b><i>SMC</i></b>              |                          |                              |                              |                          |
| 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 from treated and untreated  
 372 biomasses.  
 373

|                                | Bio-crude                |          | Solid residue            |          | Ash (wt %) |
|--------------------------------|--------------------------|----------|--------------------------|----------|------------|
|                                | Yield <sup>d</sup> (wt%) | St. dev. | Yield <sup>d</sup> (wt%) | St. dev. |            |
| <b><i>L. digitata</i></b>      |                          |          |                          |          |            |
| 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       |
| <b><i>SMC</i></b>              |                          |          |                          |          |            |
| 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 <sup>d</sup>Dry ash-free (DAF) basis  
 375

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

384

385 **Table 6** | Ultimate analysis of biocrude obtained from treated and untreated biomasses.  
 386

|                                | C (%) | H (%) | N (%) | S (%) | O (%) <sup>e</sup> |
|--------------------------------|-------|-------|-------|-------|--------------------|
| <b><i>L. digitata</i></b>      |       |       |       |       |                    |
| 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              |
| <b><i>SMC</i></b>              |       |       |       |       |                    |
| 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              |

387 <sup>e</sup> Obtained by difference between 100% and the wt% of C, H, N, S and ash.  
 388

389 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.

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

401 As far as the results from this study go, the inclusion of feedstock acid leaching is seen as a  
402 HTL enabling strategy. The fact that experiments with macroalgae and SMC at batch scale  
403 exhibited signs of potential blockage problems (i.e. major agglomeration of solids in the  
404 reactor) raise concern for the viability of continuous HTL with such feedstocks. On the other  
405 hand, biomass leaching did not lead to decreased bio-crude yields and quality. Given that cheap  
406 biomass often has a low calorific value, is of high humidity and exhibits a high content of  
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  
409 capacity to produce high quality biofuel precursors. The possibility of successfully converting  
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  
416 washing steps, whereas algae exposed to hydrochloric and sulphuric acid leaching remained at  
417 pH 5 and 4, respectively, even after 8 washing steps. Acetic, citric and sulphuric acid leached  
418 SMC reached neutral pH already after 3 washing steps, whereas hydrochloric acid pretreated  
419 biomass remained at pH 5 after 8 consecutive washing steps. Here, 3, 6 and 8 washing steps  
420 signify process water consumption levels of 0.06, 0.12 and 0.16 L for each gram of initial  
421 feedstock.

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

432

#### 433 **4 Conclusions**

434 The effects of leaching pretreatments using five different leaching agents (deionised water,  
435 acetic acid, citric acid, sulfuric acid, and hydrochloric acid) on HTL of *L. Digitata* and SMC  
436 biomass were studied. It was found that all the leaching pretreatments decreased the inorganic  
437 contents in the biomasses as expected. While, citric acid was selected as the best leaching agent  
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  
440 alternative. The results of HTL of both treated and untreated *L. Digitata* and SMC showed that  
441 the leaching treatment resulted in an increase in bio-crude yield from 20.7 to 29.2 % (dry ash-  
442 free basis) for macroalgae and from 22.9 and 25.1 % for SMC.

443

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