



25 **Abstract**

26 Microwave pyrolysis has become an attractive form of processing technology to generate bio-  
27 oil, bio-char and syngas from different biomass feedstocks. In this study, microwave pyrolysis  
28 was performed on the UK native seaweed *Laminaria digitata* and its extract residue from a  
29 bio-refinery process. Pyrolysis of these two feedstocks was successfully achieved without the  
30 requirement of microwave susceptors, as pelletizing the biomass was sufficient to allow  
31 microwave pyrolysis to occur. It was found that average energy requirements as low as 1.84 -  
32 2.83 kJ g<sup>-1</sup> were required to pyrolyse 55-70 % of both feedstocks and bio-oil yields of 5 – 8%  
33 and 10 – 14 % for native and extraction residue *L. digitata* were produced, respectively.  
34 Maximum microwave pyrolysis processing times were in the order of 200 sec. The bio-oil  
35 generated from both feedstocks contained no phenolic based compounds, but a greater number  
36 of nitrogen-containing compounds and compounds derived from macroalgal polysaccharides.  
37 Yields of certain compounds differed in bio-oils generated from the two *L. digitata* feedstocks,  
38 however it was observed that specific energy did not have a direct influence on bio-oil  
39 compound yield. Furthermore, the identification of a particular nitrogen-containing compound  
40 methyl 5-oxoprolinate is thought to be a unique product of microwave pyrolysis when carbon-  
41 based additives are avoided.

42 **KEYWORDS: Macroalgae, *Laminaria digitata*, Microwave Pyrolysis, Bio-oil, Bioenergy**

## 43 **1 Introduction**

44 The increase in fossil fuel consumption and its finite reserve has prompted research in the  
45 exploration of alternative sources to meet current and future energy demands. The legislation  
46 in this area is becoming stricter and countries within the European Union have adopted national  
47 renewable energy action plans in order to reach their own renewables target commitment [1].  
48 This includes the requirement of having at least 10% of their transportation fuels coming from  
49 renewable sources by 2020. The EU Directive on Indirect Land Use Change introduced a cap  
50 of 7% of the share of biofuels from crops grown on agricultural land to be accounted against  
51 the 10% target, and an indicative target of 0.5% for advanced biofuels by 2020 [2]. The  
52 economics of biofuel production from biomass as a primary product has been questioned  
53 mainly due to its low value [3], and as a result research in developing more holistic bio-  
54 refineries with higher value product streams is increasing. This involves the separation of  
55 biomass (as an alternative to crude oil) into its constituting fractions before being further  
56 processed into useful marketable products, with energy as a by-product [4]. However in order  
57 for bio-refinery processes to be truly sustainable, many factors need to be taken into  
58 consideration which include the choice of feedstock and the type of conversion technology that  
59 will be employed.

60 Marine macroalgae (otherwise known as seaweeds) are a third generation biomass feedstock  
61 [5], and are highly suited for bio-refinery applications due to their high value components (such  
62 as polysaccharides, proteins and bioactive molecules) and compounds that are considered to be  
63 platform chemicals for the bio-based economy (such as glucose) [6]. They do not require  
64 terrestrial land for cultivation, do not compete with food sources and have both large biomass  
65 yields and fast growth rates [7]. Bio-refinery processes which valorise the majority of the  
66 macroalgae feedstock are starting to emerge [8-14] and show the great potential of macroalgal

67 biomass as a feedstock for multiple high-value compound production. The majority of the  
68 aforementioned bio-refinery processes generally yield a residual waste material after the main  
69 target compounds of interest have either been extracted or generated via alternative  
70 methodologies (such as microbial fermentation to higher alcohols). Traditionally this waste  
71 material is either discarded or used as soil fertilizer [15] however in order for processes to align  
72 with the 12 important principals of green chemistry, the production of waste streams or residues  
73 needs to be avoided [16]. The net worth of a seaweed bio-refinery could be increased by making  
74 use of any generated waste streams from the process, and finding alternative applications to  
75 generate higher value (as opposed to fertilizers).

76 Pyrolysis is a thermo-chemical process that has attracted much attention in recent years as an  
77 economically and environmentally friendly method to process biomass [17]. Pyrolysis is the  
78 thermal decomposition of biomass (reaching temperatures between 400-600°C) in the absence  
79 of oxygen which results in the formation of three main products: bio-char, liquid bio-oil and  
80 syngas [18]. The liquid bio-oil product typically contains more than 100 oxygenated  
81 compounds which are a direct result of the thermal decomposition of the main biochemical  
82 constituents of biomass [19]. The rich chemical composition not only makes it a viable source  
83 for the thermo-chemical-based bio-refinery for the production of platform chemicals but also  
84 as a conventional biofuel [20]. Pyrolysis can be induced by conventional heating, where energy  
85 is transferred to the biomass by conduction and convection from the surface of the biomass  
86 particles. The main disadvantage of conventional pyrolysis is the slow heating rates within  
87 large particles due to the limited thermal conductivity, which consequently results in long  
88 heating times [21]. Microwave heating has become an emerging and attractive technology to  
89 use for biomass pyrolysis due to its instantaneous volumetric heating attributes, and further  
90 potential to produce a range of products which result from the unique thermal gradients [21].

91 Research on the microwave pyrolysis of macroalgae is still relatively sparse, and to date only  
92 a handful of publications can be found in which various species of macroalgae and/or  
93 macroalgal waste streams have been pyrolysed [22-25]. Macroalgae however, like most  
94 biomass feedstocks, are not efficient absorbers of microwaves due to the fact that biomass  
95 contains a mixture of different biochemical constituents that are both microwave absorbent and  
96 transparent [26]. In order to overcome this hindrance, microwave-absorbing materials such as  
97 bio-char and silicon carbide are often mixed with the biomass in order to induce pyrolysis. Yet  
98 using such additives often result in localized heating phenomena and temperatures could reach  
99 >1000°C, leading to gasification of the material instead of pyrolysis [21]. Using additives gives  
100 rise to indirect heating, where the biomass is heated by conventional heat transfer from the  
101 high-temperature additive components. In such cases the inherent advantages of microwave  
102 heating are lost.

103 The present study describes the potential of using microwave energy to pyrolyse a) the brown  
104 kelp *Laminaria digitata* (noted as ‘native’ *L. digitata*) from UK waters and b) its extraction  
105 residue obtained from the bio-process outlined in Kostas et al [13]. The residue was a direct  
106 result of the extraction of the commercially valuable phycocolloids alginate and fucoidan  
107 achieved through dilute HCl treatment. This research was not intended to represent a fully  
108 optimised microwave pyrolysis process, but to investigate several microwave pyrolysis  
109 conditions (input incident power and time) and to determine the energy required to induce  
110 microwave pyrolysis of both the native and residue *L. digitata*. Furthermore, the use of  
111 microwave absorbents was not used in this work, highlighting the significance of using  
112 microwaves directly to induce pyrolysis. The effects of incident power on biomass mass loss,  
113 bio-oil yield and quality of the two feedstocks are addressed.

## 114 **2 Materials and Methods**

### 115 **2.1 Reagents**

116 All reagents were of AnalaR grade and obtained from Sigma-Aldrich and Fisher Scientific  
117 unless otherwise specified. All water used was subjected to deionised reverse osmosis and of  
118  $\geq 18$  mega-ohm purity.

### 119 **2.2 *L. digitata* collection, preparation and production of *L. digitata* residue**

120 *L. digitata* was collected at spring low tides in May 2013 near Donderry in Cornwall  
121 (50.3623° N. 4.3687° W). The seaweed was rinsed in distilled water to remove salt and debris,  
122 and then dried in a convection oven (Genlab Oven) at 80 °C for a minimum of 48 h. The  
123 seaweed was then milled using a ball mill (Fritsch, Germany) to obtain a fine homogeneous  
124 powder and stored in a desiccator away from direct sunlight and moisture until further use. The  
125 *L. digitata* extraction residue used in this study was produced from the bio-process outlined in  
126 the paper by Kostas et al [13].

### 127 **2.3 Characterisation of *L. digitata***

#### 128 **2.3.1 Multi Element Analysis**

129 Native *L. digitata* and extraction residue (200 mg) were weighed into digestion vessels to which  
130 6 mL of HNO<sub>3</sub> (concentrated) was added. The digestion vessels were then placed into a  
131 microwave rotor (Anton Paar Multiwave Pro 24HVT50) where they were heated to 140°C for  
132 20 min and then cooled at 55°C for 15 min. Once the digestion was complete, Milli-Q H<sub>2</sub>O  
133 was added to make a final volume of 20 mL. Samples were then transferred to a universal  
134 storage bottle and stored at 4°C until analysis. For the quantification of iodine, samples were  
135 prepared according to the method of Watts and Mitchell [27]. Samples (250 mg) were weighed  
136 into Pyrex tubes, to which 5 mL of 5% (v/v) Tetramethylammonium hydroxide (TMAH) was  
137 added. Samples were shaken before being placed into a convection oven at 70°C for 3 h, with

138 bottles shaken at 1.5 h. DI water (5 mL) was added to the samples after the 3 h incubation  
139 period, and the samples were transferred to 50 mL centrifuge tubes and centrifuged at 2500  
140 rpm for 25 min. The supernatant was diluted to a final concentration of 1% (v/v). All analyses  
141 were conducted in triplicate.

142 All trace multi-element analysis was performed on an ICP-MS (Thermo-Fisher iCAP-Q)  
143 equipped with a Flatpole collision cell upstream of the analytical quadrupole to reduce  
144 polyatomic interferences. Internal standards were introduced to the sample stream via a T-piece  
145 and typically included Sc (50  $\mu\text{g L}^{-1}$ ), Ge (20  $\mu\text{g L}^{-1}$ ), Rh (10  $\mu\text{g L}^{-1}$ ) and Ir (5  $\mu\text{g L}^{-1}$ ) in the  
146 preferred matrix of 2%  $\text{HNO}_3$ . External calibration standards were all in the range 0 – 100  $\mu\text{g}$   
147  $\text{L}^{-1}$ . Samples were introduced via a covered autosampler (Cetac ASX-520) through a  
148 concentric glass venturi nebuliser (Thermo-Fisher Scientific) or a PEEK Burgener Miramist  
149 nebuliser. Sample processing was undertaken using Qtegra software (Thermo-Fisher  
150 Scientific).

### 151 **2.3.2 Thermal Characterisation**

152 Thermal profiles were obtained using TA Instruments Q5000 TGA (New Castle, DE, USA)  
153 according to the method outlined in Lester et al [28]. Samples (10-15 mg) were placed in  
154 alumina pans and heated from room temperature to 900  $^{\circ}\text{C}$  at 5  $^{\circ}\text{C min}^{-1}$  with a nitrogen flowrate  
155 of 100  $\text{ml min}^{-1}$ . At 900  $^{\circ}\text{C}$  the gas was switched to air at 100  $\text{ml min}^{-1}$ .

156 The dry Higher Heating Value (HHV) of the two were found using an IKA C5000 Bomb  
157 Calorimeter (Staufen, Germany) in accordance with BS ISO 1928:2009 [29]. IKA certified  
158 benzoic acid tablets were used as a standard and the sample weight was calibrated to give the  
159 same temperature rise as the standard. Moisture content was obtained from thermo-gravimetric  
160 analysis. Mass yield ( $m_y$ ) and energy yield ( $E_y$ ) were calculated as follows:

$$161 \quad m_y = \frac{m_b}{m_a} \cdot 100\% \quad (1)$$

162 
$$E_y = m_y \cdot \frac{HHV_b}{HHV_a} \cdot 100\% \quad (2)$$

163 Where  $m_a$  is the mass of the raw samples (g),  $m_b$  is the mass of the microwave treated samples  
164 (g),  $HHV_a$  is the higher heating value of the raw samples ( $J g^{-1}$ ), and  $HHV_b$  is the higher heating  
165 value of the microwave treated samples (J/g).

### 166 **2.3.3 Dielectric properties**

167 The dielectric constant ( $\epsilon'$ ) and dielectric loss factor ( $\epsilon''$ ) of the native and residue *L. digitata*  
168 were determined using the cavity perturbation technique. The measurements were performed  
169 at 2470 MHz, from 20 to 600 °C. The resonant cavity consists of a cylindrical copper cavity  
170 connected to a vector network analyser, which measures the frequency shift and change in  
171 quality factor relative to the empty resonating cavity when a sample is introduced. The seaweed  
172 samples were loaded into a quartz tube, and held in a conventionally heated furnace above the  
173 cavity until the temperature set-point was reached. The tube was then moved into the cavity to  
174 make the measurement at the required temperature. A detailed description of the equipment is  
175 given by Adam et al [30].  $\epsilon'$  is a measure of a material's ability to store electromagnetic energy  
176 through polarisation, and  $\epsilon''$  is a material's ability to convert this stored energy into heat [31].  
177  $\epsilon'$  and  $\epsilon''$  can be used to assess the general ability of a material to heat in an electromagnetic  
178 field, and this quantity is known as the loss tangent,  $\tan \delta$ :

179 
$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad (3)$$

### 180 **2.4 Microwave pyrolysis experiments**

181 Prior to the microwave pyrolysis trials the seaweed samples were densified in a 20 ton Specac  
182 automatic pellet press. Samples (10 g) were loaded into a 31.75 mm pellet die and loaded to 8  
183 tons of pressure. Average native and residue pellet densities were  $1355 \pm 43 \text{ kg/m}^3$  and  $1308 \pm$   
184  $45 \text{ kg/m}^3$  respectively.



185 The microwave pyrolysis system used in the present study is shown in Fig 1. The system was  
186 operated at frequency of  $2450 \pm 25$  MHz and includes a generator with 2 kW maximum output  
187 power; an automatic three-stub tuner (S-TEAM STHD v1.5) connected to a rectangular WR430  
188 waveguide. The automatic tuner was used for impedance matching, to minimise the reflected  
189 power and also to log the absorbed power over time so the specific absorbed energy could be  
190 calculated [32]. A cylindrical single mode TE<sub>010</sub> cavity was connected by WR430 waveguide  
191 to the sliding short and the incident, absorbed and reflected powers were recorded. The  
192 pyrolysis reactor consisted of a quartz tube (35 mm ID) where the pelletized sample was placed.  
193 Before performing any pyrolysis experiments, optimal tuner settings were determined using a  
194 vector network analyser and adjusting the stub and sliding-short positions to minimise reflected  
195 power. The heating system was calibrated with no sample present to confirm <5% power loss  
196 to the waveguide and reactor walls. Since it is not possible to obtain accurate temperature  
197 measurements in microwave-heating experiments [33, 34], absorbed energy was used instead  
198 of temperature as a control variable.

199 The system was purged with nitrogen for 5 min before performing the pyrolysis experiments  
200 (Fig. 1). Once the system was purged, the nitrogen flow rate was set to 10 ml/min. Incident  
201 powers (180-650 W) and pyrolysis times (20-160 sec) were varied to establish suitable  
202 pyrolysis parameters on the native *L. digitata* samples. The vapours produced during pyrolysis  
203 were quenched by a condenser and bio-oil was collected in a flask and stored at 4°C until  
204 further analysis. Any non-condensables were vented through an extraction system. The solid  
205 (bio-char) which remained at the end of the trials was collected and weighed to calculate the  
206 percentage mass loss.

207 The percent of absorbed and reflected power was calculated from the signals of incident power,  
208 absorbed power and reflected power. The specific absorbed energy (E) was determined by

209 numerical integration of the absorbed power, ( $P_a$ ), over time according to the following  
210 equation:

$$211 \quad E = \frac{\int P_a dt}{M} \quad (2)$$

212 Where  $E$  is the specific absorbed energy ( $\text{kJ g}^{-1}$ ),  $dt$  is the time differential (sec) and  $M$  is the  
213 initial mass of the pellet (g).

214 The most suitable incident power that produced the greatest yield of bio-oil and highest mass  
215 loss for the native *L. digitata* was selected for further pyrolysis trials using the *L. digitata*  
216 extraction residue. This was explored with varying pyrolysis run times (80 – 200 sec).

## 217 **2.5 Pyrolytic product analysis**

218 As the current study is limited only to identifying the properties of bio-oil and bio-char products  
219 of the process, the bio-gas fraction was not collected and no analytical tests for the gaseous  
220 product was conducted. Bio-oil samples were analysed by Gas-Chromatography Mass-  
221 Spectrometry (JEOL GCX time-of-flight GC-MS; JEOL Ltd., Tokyo, Japan). The injection  
222 port temperature of the GC was set at 200°C and was operated in splitless mode. The GC  
223 column used was a ThermoFisher Scientific TG-POLAR (ThermoFisher Scientific,  
224 Massachusetts, USA) capillary column (30 m x 0.25 mm, 0.25  $\mu\text{m}$  stationary phase thickness).  
225 Helium was used as the carrier gas, at a flow rate of 1.5  $\text{mL min}^{-1}$ . The GC oven was heated  
226 from 40°C (hold 3 min) to 260°C at a rate of 5°C  $\text{min}^{-1}$ . The GC interface was held at 240°C,  
227 while the mass spectrometer ion source was heated to 280°C. Components eluting from the GC  
228 were ionized by electrons of 70 eV energy and their mass spectra recorded by the TOF-MS.  
229 The area percentage method was used for the quantification of the compounds present in the  
230 bio-oil. Identification of individual compounds was performed by comparing experimental  
231 mass spectra with those in the NIST Mass Spectral library (NIST14 database; National Institute  
232 of Standards and Technology, Maryland, USA).

## 233 **3 Results and Discussion**

### 234 **3.1 Biochemical Characterisation**

235 The gross composition of the seaweed samples used in this study was as previously reported  
236 [13] and can be seen in Table 1. Analysis indicated that the recovery of fucoidan and alginate  
237 did alter the biochemical composition, and an enrichment of the crude fibre content (5.5% (d/w)  
238 in native to 15.5% (d/w) in the residue) was noticeable.

239 The concentrations of the main elements in the native *L. digitata* and extraction residue are  
240 shown in Fig 2. The level of potassium was enriched in the residue and was the most abundant  
241 of the elements quantified ( $14149.0 \pm 679.2 \text{ mg kg}^{-1}$ ). Macroalgae in general are known to be  
242 a significant source of minerals due to their ability to uptake inorganic substances from the  
243 environment they inhabit and store these elements in their cell walls [35]. Biomass contains a  
244 mixture of phases that are both microwave absorbent and microwave transparent, and their  
245 heterogeneous nature needs to be understood when using microwaves for thermal-based  
246 processes. It is therefore vital to have an understanding of biomass elemental composition for  
247 studies such as this, particularly since metal ions are known to be good absorbers of  
248 microwaves.

### 249 **3.2 Thermal and Dielectric Characterisation**

250 The thermal and dielectric profiles of native *L. digitata* and extraction residue can be seen in  
251 Figs. 3 a and b. The loss tangent for the dielectric profile is a highly non-linear function of  
252 temperature for both biomasses, with peaks observed at 100°C and 250°C, and a large rate of  
253 increase at temperatures in excess of 500°C. The measured dielectric properties are a result of  
254 both dipolar and ionic interactions with the electric field, and also chemical transformations  
255 within the biomass as the temperature increases. The behaviour of the dielectric properties can  
256 be related to mass loss resulting from volatilisation of the *L. digitata* samples, as decomposition

257 peaks are evident at 237°C and 234°C for the native seaweed and extraction residue,  
258 respectively (Fig. 3b). From 300°C the loss tangent remains relatively low up to 500°C  
259 matching the end of the peak volatile losses, which explains the use of microwave-absorbing  
260 additives in previous studies [36-39]. No microwave susceptors are used in this study so the  
261 observed products are due to direct interactions of microwaves with the seaweed and not due  
262 to localised high temperatures caused by high-loss additives. Instead, the study uses equipment  
263 with a well-defined electric field distribution and an impedance matching device. After 500°C  
264 the sample essentially becomes char, resulting in an exponential increase in the loss tangent  
265 due to the increases of conductivity caused by the high displacement of  $\pi$ -electrons in the  
266 carbonized structure [40].

### 267 **3.3 Microwave Pyrolysis Trials**

#### 268 **3.3.1 Incident Power and Absorbed Energy**

269 Published literature on microwave pyrolysis of biomass has typically used microwave devices  
270 that cannot measure reflected power. In such cases it is impossible to determine the amount of  
271 energy absorbed by the sample [26], making it difficult to compare between different studies  
272 and requiring that results be interpreted with caution.

273 Biomass is known to be a relatively poor absorber of microwave energy compared to water for  
274 example which has a loss tangent of 0.17 at room temperature [41]. Referring to Fig 3, the loss  
275 tangents of both native *L. digitata* and extraction residue (Fig 3 a) are at their lowest at 350-  
276 500°C, which is the temperature required to induce pyrolysis [42]. Figs 4 a, b and c clearly  
277 show that microwaves can be absorbed by the densified samples. Fig 4a shows an example of  
278 the incident microwave power (average 180 W) that was supplied to both the native *L. digitata*  
279 and extraction residue for 80 sec in the microwave pyrolysis system. It is evident that not all  
280 of the incident power was absorbed and there was some degree of reflected power by both  
281 samples. For the native *L. digitata*, an average of 76% of the incident power was absorbed and

282 24% was reflected, while the *L. digitata* extraction residue absorbed an average of 59% and  
283 reflected 41% (Fig 4 b and c). These trends are in agreement with the loss tangent values at  
284 temperatures above 250°C, where the native sample is a (slightly) stronger absorber of  
285 microwaves (Fig 3 a). Differences in inorganic metal elements between the two samples are  
286 likely to be a contributing factor and it has been reported that sodium and potassium ions have  
287 catalytic effects on the pyrolysis process of macroalgae [43]; elements of which were identified  
288 in high abundance in the *L. digitata* samples and in particular potassium in the extraction  
289 residue (Fig 2). It is evident that for both the native seaweed and extraction residue, a minimum  
290 of 25 sec and 35 sec are needed in order to achieve the highest percentage of absorbed  
291 microwave power (with the lowest incident power tested in this study; 180W).

### 292 3.3.2 *Native L. digitata Microwave Trials*

293 The first set of experiments sought to investigate the microwave pyrolysis potential of the  
294 native *L. digitata* material and whether incident power and heating time had an influence on  
295 mass loss and bio-oil yield. In order to make the trials directly comparable, the absorbed energy  
296 for each microwave pyrolysis experiment was calculated (see Section 2.4 Eq. 2) and mass loss  
297 (%) and bio-oil yield (%) were determined. Absorbed energy is a secondary measured variable  
298 that cannot be directly controlled, but it is used instead of temperature due to the uncertainties  
299 associated with temperature measurement within a microwave environment [26, 44],  
300 particularly when fixed-beds are used [30, 45]. Furthermore, thermocouples embedded within  
301 a microwave reactor can distort microwave fields and conduct heat away from the sample, thus  
302 inducing thermal instabilities and microwave breakdown [33, 46].

303 Fig 5 a and b show the impact of varying absorbed energy on the mass loss of native *L. digitata*  
304 and bio-oil yields produced. The pellets post processing can be also seen in Figs 6 a to d which  
305 depicts an increase in the degree of pyrolysis on the native *L. digitata* pellets as the specific  
306 energy increases (0 – 2.7 kJ g<sup>-1</sup>) compared to the starting material. The densification has led to

307 a concentration of the microwave heating in the centre of the pellet. The system was designed  
308 so that the microwave energy would target the biomass pellet, whose bound and surface water  
309 has the high dielectric properties [47]. It appeared that at higher energies it is possible to obtain  
310 a greater mass loss and higher oil yield, which most likely results from a more efficient thermal  
311 biomass decomposition as higher temperatures are achieved. For example, energy values  
312 between 1.6 – 3.0 kJ g<sup>-1</sup> achieved mass losses between 50 – 70 % and bio-oil yields within the  
313 ranges of 9 - 15 % (Fig 5 a and b). This phenomenon was also reported in the works of Robinson  
314 et al [21] and Adam et al [45]. Previous studies have shown a beneficial effect of power at  
315 equivalent energy input, however it is apparent from Fig 5 that energy alone has the dominant  
316 effect on bio-oil yield.

### 317 **3.3.3 *L. digitata* Residue Microwave Trials**

318 From Figs 5 a and 5 b an incident power of 180 W appeared to be the most suitable input power  
319 to pyrolyse the seaweed whilst giving the highest liquid yield. This power was subsequently  
320 selected for trials using the extraction residue samples. Results on mass loss and obtained bio-  
321 oil yields are seen in Figs 7 a and b in comparison with the native *L. digitata* at the same  
322 incident power. It is evident that there is a similar mass loss trend between the two samples;  
323 pyrolysing for longer times as seen in Fig 7 by the increase in specific absorbed energy results  
324 in higher degrees of mass loss. Similarly, as seen in Figs 6 a to d, an increase in specific energy  
325 (from 0 to 2.8 kJ g<sup>-1</sup>) pyrolyses a greater proportion of the *L. digitata* extraction residue pellet  
326 and volumetric heating of the pellets is evident (Figs 8 a to d). Specific absorbed energies above  
327 1.6 kJ g<sup>-1</sup> results in mass losses of ≥ 45% for both native and residue *L. digitata*. These results  
328 correlate with the yields of bio-oil obtained in Fig 7 b.

329 Specific energies lower than 1.4 kJ g<sup>-1</sup> resulted in the production of no bio-oil from the residue  
330 *L. digitata* despite the fact that mass losses of around 10 – 30 % were obtained. This could be

331 a result of the pellet not being pyrolysed for a sufficient amount of time that would be normally  
332 required to induce volumetric heating and produce condensable vapours which would be  
333 quenched directly to bio-oil. Therefore, the required bio-oil production threshold was not  
334 reached at this specific energy. For both seaweed samples, specific energies above 1.5 kJ g<sup>-1</sup> to  
335 around 2.3 kJ g<sup>-1</sup> produced greater yields of bio-oil; between 5 – 10 % and 3 to 10 % for the  
336 native *L. digitata* and residue *L. digitata*, respectively. Increasing the amount of energy  
337 supplied to the samples leads to higher temperatures, therefore greater levels of thermal  
338 decomposition would be expected. Overall, bio-oil yields were lower for the residue *L digitata*  
339 which could be a result from the differences in biochemical composition (Table 1) [13].

340 Above 2.5 kJ g<sup>-1</sup>, both seaweed samples reached mass losses as high as 60 %. It is evident  
341 however that there are distinct differences in the yields of bio-oil produced from both native  
342 and residue *L. digitata* feedstocks at this particular specific energy. Around 15 % bio-oil yield  
343 was obtained from native *L. digitata* whereas only 5 % was produced from the residue,  
344 suggesting that an energy value of 2.5 kJ g<sup>-1</sup> may not be compatible with the residue for bio-  
345 oil production. This could be due to the higher heating rate inducing temperatures greater than  
346 the requirement for pyrolysis and essentially producing non-condensable gases via gasification.  
347 Despite the fact that syngas is an additional source of bioenergy, it was not quantified in this  
348 study as it was beyond scope. However, incorporating syngas production from seaweeds in  
349 future studies would enhance the overall life cycle/techno-economical analysis of this process.

### 350 **3.4 Energy yield of native *L. digitata* and extraction residue bio-chars**

351 The energy yield of the biomass indicates the total energy preserved during the microwave  
352 pyrolysis process. Fig 9 shows the variation of energy yield for the native and residue *L.*  
353 *digitata* bio-char samples for increasing specific absorbed energies. There is a linear correlation  
354 between specific absorbed energy and the reduction in energy yield, which has been noted in

355 several previous microwave pyrolysis studies [48]. The *L. digitata* residue bio-chars have  
356 higher initial energy yields compared to the native *L. digitata* bio-chars, but the values  
357 converge for specific absorbed energies over 1.5 kJ kg<sup>-1</sup>. The decline in energy yield is due to  
358 the sharp decrease in mass yield for samples which are exposed to higher specific absorbed  
359 energies (Fig. 7a). The results indicate that *L. digitata* residue samples conserve more energy  
360 during the microwave pyrolysis process than the native *L. digitata* samples, but severe  
361 pyrolysis conditions may result in larger mass and energy yield losses.

### 362 **3.5 Characterisation of bio-oil samples from native *L. digitata* and extraction residue**

363 Bio-oil generated from biomass feedstocks via pyrolysis contains a large number of oxygenated  
364 compounds with reactive functional groups, which makes its complete characterisation often a  
365 challenging and tedious task. However, recent advances in bio-oil analysis have been made,  
366 such as comprehensive two-dimensional gas chromatography and even the use of a time-of-  
367 flight mass spectrometer that has led to a dramatic improvement of qualitative analysis [49]. In  
368 this study, bio-oils that were successfully produced from both the native *L. digitata* and  
369 extraction residue at different specific energies were analysed by GC-MS. Due to the high  
370 number of peaks found on the GC-MS chromatograms and difficulties separating the peaks due  
371 to the complex composition of bio-oil, a number of compounds were semi quantitatively  
372 evaluated and can be seen in Table 2. Peaks that had a high degree of certainty (over 85 %) are  
373 included. It is evident that the bio-oils produced from the MW pyrolysis of the two *L. digitata*  
374 feedstocks at different specific energies contained a mixture of different hydrocarbons,  
375 aldehydes, ketones, alcohols, nitrogen-containing compounds and sugar alcohols. As expected,  
376 no identifiable compounds are phenol based since these compounds are typically derived from  
377 the lignin constituent of lignocellulosic biomass. A previous study undertaken by Robinson et  
378 al [21] which used similar equipment to pyrolyse Larch woodchips (*Larix decidua*) yielded  
379 bio-oil that contained significant amounts of phenols (namely phenol, eugenol, catechol and



380 creosol) and the anhydrosugar levoglucosan, of which is somewhat expected for bio-oil derived  
381 from lignocellulosic biomass. On the contrary it is evident that the bio-oils produced herein are  
382 mainly comprised of pyrolytic degradation products from macroalgal specific polysaccharides  
383 and proteins which make up the main composition constituents of this type of biomass, and a  
384 handful of these compounds (including dianhydromannitol, isosorbide, 2-hydroxy-3-methyl-  
385 2-cyclopentene-1-one, 1-(2-furanyl)-ethanone, 2-furanmethanol and 2,3 - dimethyl-2-  
386 cyclopentene-1-one) have been previously identified as major pyrolysis products of brown  
387 macroalgae [50-53]. Specifically, dianhydromannitol and isosorbide are compounds derived  
388 from the thermal degradation of the polysaccharide laminarin and the sugar alcohol mannitol  
389 [54]. These sugars are uniquely inherent to brown species of macroalgae and it is evident that  
390 these compounds are more abundant in bio-oils produced from the native *L. digitata* which had  
391 not undergone an extraction process. Additionally, 1-(2-furanyl)-ethanone, a thermal product  
392 from the degradation of alginate [54], is more prevalent in bio-oils generated from native *L.*  
393 *digitata* (3.94 - 6.06 %) and not as abundant in bio-oils from the extraction residue (0.79 – 1.57  
394 %). This is expected since alginate was the first extracted product from the bio-process [13]. It  
395 appears that specific energy also influences the yield of 1-(2-furanyl)-ethanone present in bio-  
396 oils generated from both native *L. digitata* and residue. This also appears to apply for nitrogen-  
397 containing compounds azetidine-1-carboxaldehyde and 4-methyl-1, 2, 4-triazol-3-amine,  
398 where despite the overall percentage areas of these compounds are higher in bio-oils generated  
399 from native *L. digitata*, the differences in percentage area vary according to specific energy.  
400 On the contrary, methyl 5-oxoprolinate (additionally a nitrogen-containing compound) that  
401 was identified in high abundance in all generated bio-oils, did not appear to vary with energy  
402 input. However, the percentage areas of methyl 5-oxoprolinate are slightly higher in bio-oils  
403 generated from the *L. digitata* residue compared to the native feedstock. This could be a result  
404 of the enriched protein fraction in the residue as previously characterised in the works of Kostas

405 et al [13] (seen in Table 1) which had thermally decomposed during the pyrolysis process to  
406 yield methyl 5-oxoprolinate. The presence of nitrogen-containing compounds in bio-oils  
407 produced from macroalgal pyrolysis has been previously reported and are often present in  
408 higher abundance compared to lignocellulosic bio-oils [23, 52, 54, 55]. A study by Wang et al  
409 [43] investigated the (conventional) pyrolytic mechanisms of macroalgal biochemical  
410 constituents suggested that the temperature at which seaweed proteins start to pyrolyse is within  
411 the range of ~300 to 350°C, and has been speculated that the fracture and decarboxylation of  
412 amino acids from proteins begin at around 300°C. This is the first study however, to report  
413 methyl 5-oxoprolinate (derived from the amino acid proline) in pyrolysis bio-oils and it may  
414 be a characteristic product of microwave pyrolysis. Previous studies using conventional  
415 pyrolysis did not detect this compound, and neither did Ferrera-Lorenzo [23] in their study that  
416 involved the microwave pyrolysis of a waste product of the red macroalgae *Gelidium spp.* A  
417 possible reason other studies have not detected this compound could be due to inherently higher  
418 temperatures within their experimental setups. Ferrera-Lorenzo [23] used char as a microwave-  
419 absorbing additive within their setup, which results in selective heating of the char and heat  
420 transfer to the macroalgae by conventional means. In this case there is a large temperature  
421 gradient within the bed of material, and areas of very high temperature. Macroalgal pyrolysis  
422 products that are evolved into this high temperature environment will therefore undergo further  
423 thermal decomposition. Conventional pyrolysis processes exhibit a similar effect as the entire  
424 reactor temperature is maintained ~500°C. When microwave pyrolysis is achieved without  
425 adding carbon-based additives, as in this study, the environment that surrounds the macroalgae  
426 is kept at a low temperature due to the presence of the cold nitrogen sweep gas and in effect  
427 prevents further thermal decomposition of primary bio-oil compounds. A similar but not  
428 directly comparable microwave pyrolysis system developed by Shepherd et al [56], uses a  
429 liquid inerting phase (instead of gas) at atmospheric pressure which acts as a direct heat-sink.

430 The aforementioned study proved that the generated bio-oil compounds did not suffer extensive  
431 thermal degradation due to the presence of a cold liquid surrounding the biomass whilst being  
432 pyrolysed. This highlights a key difference between microwave and conventional pyrolysis, as  
433 the electric field provides the energy directly to the biomass and the presence of cooler  
434 surroundings will yield bio-oils containing alternative compounds. Above 300°C, single amino  
435 acid molecules can thermally degrade and generate amino acid derived compounds via  
436 different mechanisms and reaction pathways [43]. It is thought therefore that the primary  
437 decomposition mechanisms of seaweed constituents (and in this case protein) are the same  
438 irrespective of the heating method used, but the additive-free microwave pyrolysis route  
439 promotes the preservation of primary pyrolysis products. The high observed yield of methyl 5-  
440 oxoprolinate is likely to be due to the inherent low temperature of the microwave pyrolysis  
441 system used in this work which explains its generation via an additive free route and presence  
442 in microwave pyrolysis bio-oils. Further research is required to compare the products found in  
443 bio-oils generated from native and residue *L. digitata* via both microwave and conventional  
444 heating means in order to establish whether bio-oils of different functionalities could be  
445 produced by exploiting this low-temperature process pathway, and ultimately elucidate feasible  
446 degradation pathways for the different bio-constituents in macroalgae. In addition, the absence  
447 of phenol based compounds and high abundance of nitrogen-containing derived compounds in  
448 the pyrolysis bio-oils essentially makes this bio-oil a ‘microbe-friendly’ substrate which opens  
449 the avenue of direct downstream processing via microorganisms for high value product  
450 generation.

#### 451 **4 Conclusions**

452 Microwave pyrolysis of native *L. digitata* and its residue generated from an extraction process  
453 was successfully achieved without the need to add microwave susceptors. Pelletizing the  
454 biomass was sufficient to allow microwave pyrolysis to occur when using a single mode cavity.

455 Average energy requirements of 1.84 - 2.83 kJ g<sup>-1</sup> were needed to pyrolyse 55-70 % of both *L.*  
456 *digitata* feedstocks, where maximum microwave heating times were in the order of 200  
457 seconds. The yield of bio-oil produced under these conditions was 5 – 8% and 10 – 14 % for  
458 native and residue *L. digitata*, respectively. Analysis of the generated bio-oils from both  
459 feedstocks revealed the presence of no phenolic based compounds, but an abundance of  
460 nitrogen-containing compounds and compounds derived from the thermal breakdown of brown  
461 macroalgal polysaccharides. The low oil yield does not favour direct use for bioenergy,  
462 however the oil phase contained up to 87 % of a single compound; methyl 5-oxoprolinate. This  
463 compound was not identified in previous studies and is thought to be a unique product of  
464 microwave pyrolysis when carbon-based additives are avoided. Furthermore work will aim to  
465 establish and compare differences between the thermal decomposition mechanism of seaweed  
466 proteins and polysaccharides achieved via conventional heating and this novel additive-free  
467 microwave pyrolysis route.

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