Microwave pyrolysis of *Laminaria digitata* to produce unique seaweed-derived bio-oils

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26 **Abstract**

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

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

44 ## 1 Introduction

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

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

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

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

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

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

115 ## 2 Materials and Methods

116 ### 2.1 Reagents

117 All reagents were of AnalaR grade and obtained from Sigma-Aldrich and Fisher Scientific
118 unless otherwise specified. All water used was subjected to deionised reverse osmosis and of
119 ≥18 mega-ohm purity.

120 ### 2.2 *L. digitata* collection, preparation and production of *L. digitata* residue

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

128 ### 2.3 Characterisation of *L. digitata*

129 #### 2.3.1 Multi Element Analysis

130 Native *L. digitata* and extraction residue (200 mg) were weighed into digestion vessels to which
131 6 mL of HNO_3 (concentrated) was added. The digestion vessels were then placed into a
132 microwave rotor (Anton Paar Multiwave Pro 24HVT50) where they were heated to 140°C for
133 20 min and then cooled at 55°C for 15 min. Once the digestion was complete, Milli-Q H_2O
134 was added to make a final volume of 20 mL. Samples were then transferred to a universal
135 storage bottle and stored at 4°C until analysis. For the quantification of iodine, samples were
136 prepared according to the method of Watts and Mitchell [27]. Samples (250 mg) were weighed
137 into Pyrex tubes, to which 5 mL of 5% (v/v) Tetramethylammonium hydroxide (TMAH) was
138 added. Samples were shaken before being placed into a convection oven at 70°C for 3 h, with

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

143 All trace multi-element analysis was performed on an ICP-MS (Thermo-Fisher iCAP-Q)
144 equipped with a Flatopole collision cell upstream of the analytical quadrupole to reduce
145 polyatomic interferences. Internal standards were introduced to the sample stream via a T-piece
146 and typically included Sc (50 µg L^{-1}), Ge (20 µg L^{-1}), Rh (10 µg L^{-1}) and Ir (5 µg L^{-1}) in the
147 preferred matrix of 2% HNO_3. External calibration standards were all in the range 0 – 100 µg
148 L^{-1}. Samples were introduced via a covered autosampler (Cetac ASX-520) through a
149 concentric glass venturi nebuliser (Thermo-Fisher Scientific) or a PEEK Burgener Miramist
150 nebuliser. Sample processing was undertaken using Qtegra software (Thermo-Fisher
151 Scientific).

152 **2.3.2 Thermal Characterisation**

153 Thermal profiles were obtained using TA Instruments Q5000 TGA (New Castle, DE, USA)
154 according to the method outlined in Lester et al [28]. Samples (10-15 mg) were placed in
155 alumina pans and heated from room temperature to 900 ºC at 5 ºC min^{-1} with a nitrogen flowrate
156 of 100 ml min^{-1}. At 900 ºC the gas was switched to air at 100 ml min^{-1}.
157 The dry Higher Heating Value (HHV) of the two were found using an IKA C5000 Bomb
158 Calorimeter (Staufen, Germany) in accordance with BS ISO 1928:2009 [29]. IKA certified
159 benzoic acid tablets were used as a standard and the sample weight was calibrated to give the
160 same temperature rise as the standard. Moisture content was obtained from thermo-gravimetric
161 analysis. Mass yield (m_y) and energy yield (E_y) were calculated as follows:

162 $$m_y = \frac{m_b}{m_a}.100\% \quad (1)$$

163 $$E_y = m_y.\frac{HHV_b}{HHV_a}.100\%$$ (2)

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

167 ### 2.3.3 Dielectric properties

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

180 $$\tan\delta = \frac{\varepsilon''}{\varepsilon'}$$ (3)

181 ## 2.4 Microwave pyrolysis experiments

182 Prior to the microwave pyrolysis trials the seaweed samples were densified in a 20 ton Specac
183 automatic pellet press. Samples (10 g) were loaded into a 31.75 mm pellet die and loaded to 8
184 tons of pressure. Average native and residue pellet densities were 1355 ± 43 kg/m^3 and 1308 ±
185 45 kg/m^3 respectively.

186 The microwave pyrolysis system used in the present study is shown in Fig 1. The system was
187 operated at frequency of 2450 ± 25MHz and includes a generator with 2kW maximum output
188 power; an automatic three-stub tuner (S-TEAM STHD v1.5) connected to a rectangular WR430
189 waveguide. The automatic tuner was used for impedance matching, to minimise the reflected
190 power and also to log the absorbed power over time so the specific absorbed energy could be
191 calculated [32]. A cylindrical single mode TE_{010} cavity was connected by WR430 waveguide
192 to the sliding short and the incident, absorbed and reflected powers were recorded. The
193 pyrolysis reactor consisted of a quartz tube (35 mm ID) where the pelletized sample was placed.
194 Before performing any pyrolysis experiments, optimal tuner settings were determined using a
195 vector network analyser and adjusting the stub and sliding-short positions to minimise reflected
196 power. The heating system was calibrated with no sample present to confirm <5% power loss
197 to the waveguide and reactor walls. Since it is not possible to obtain accurate temperature
198 measurements in microwave-heating experiments [33, 34], absorbed energy was used instead
199 of temperature as a control variable.
200 The system was purged with nitrogen for 5 min before performing the pyrolysis experiments
201 (Fig. 1). Once the system was purged, the nitrogen flow rate was set to 10 ml/min. Incident
202 powers (180-650 W) and pyrolysis times (20-160 sec) were varied to establish suitable
203 pyrolysis parameters on the native *L. digitata* samples. The vapours produced during pyrolysis
204 were quenched by a condenser and bio-oil was collected in a flask and stored at 4°C until
205 further analysis. Any non-condensables were vented through an extraction system. The solid
206 (bio-char) which remained at the end of the trials was collected and weighed to calculate the
207 percentage mass loss.
208 The percent of absorbed and reflected power was calculated from the signals of incident power,
209 absorbed power and reflected power. The specific absorbed energy (E) was determined by

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

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

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

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

218 2.5 Pyrolytic product analysis

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

234 # 3 Results and Discussion

235 ## 3.1 Biochemical Characterisation

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

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

250 ## 3.2 Thermal and Dielectric Characterisation

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

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

268 **3.3 Microwave Pyrolysis Trials**

269 **3.3.1 Incident Power and Absorbed Energy**

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

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

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

293 ***3.3.2 Native L. digitata Microwave Trials***

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

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

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

318 ***3.3.3 L. digitata Residue Microwave Trials***

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

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

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

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

351 ***3.4 Energy yield of native L. digitata and extraction residue bio-chars***

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

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

363 ### ***3.5 Characterisation of bio-oil samples from native L. digitata and extraction residue***

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

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

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

431 liquid inerting phase (instead of gas) at atmospheric pressure which acts as a direct heat-sink.
432 The aforementioned study proved that the generated bio-oil compounds did not suffer extensive
433 thermal degradation due to the presence of a cold liquid surrounding the biomass whilst being
434 pyrolysed. This highlights a key difference between microwave and conventional pyrolysis, as
435 the electric field provides the energy directly to the biomass and the presence of cooler
436 surroundings will yield bio-oils containing alternative compounds. Above 300°C, single amino
437 acid molecules can thermally degrade and generate amino acid derived compounds via
438 different mechanisms and reaction pathways [43]. It is thought therefore that the primary
439 decomposition mechanisms of seaweed constituents (and in this case protein) are the same
440 irrespective of the heating method used, but the additive-free microwave pyrolysis route
441 promotes the preservation of primary pyrolysis products. The high observed yield of L-Proline,
442 1-methyl-5-oxo-, methylester is likely to be due to the inherent low temperature of the
443 microwave pyrolysis system used in this work which explains its generation via an additive
444 free route and presence in microwave pyrolysis bio-oils. Further research is required to
445 compare the products found in bio-oils generated from native and residue *L. digitata* via both
446 microwave and conventional heating means in order to establish whether bio-oils of different
447 functionalities could be produced by exploiting this low-temperature process pathway, and
448 ultimately elucidate feasible degradation pathways for the different bio-constituents in
449 macroalgae. In addition, the absence of phenol based compounds and high abundance of
450 nitrogen-containing derived compounds in the pyrolysis bio-oils essentially makes this bio-oil
451 a 'microbe-friendly' substrate which opens the avenue of direct downstream processing via
452 microorganisms for high value product generation.

453 4 Conclusions

454 Microwave pyrolysis of native *L. digitata* and its residue generated from an extraction process
455 was successfully achieved without the need to add microwave susceptors. Pelletizing the

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

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