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

Emily T. Kostas[1§], Orla S. A. Williams[1], Gabriela Duran-Jimenez[1], Andrew J. Tapper[1], Mick Cooper[2], Richard Meehan[2], John P. Robinson[1]

[1]Faculty of Engineering, the University of Nottingham, University Park, Nottingham, NG7 2RD, U.K.

[2]School of Chemistry, the University of Nottingham, University Park, Nottingham, NG7 2RD, U.K.

TITLE RUNNING HEAD: Microwave pyrolysis of *Laminaria digitata*

§ Corresponding author

e-mail: emily.kostas@nottingham.ac.uk

Tel: +44 (0)115 9514080

Abstract

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

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

1 Introduction

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

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

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

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

2 Materials and Methods

2.1 Reagents

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

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

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

2.3 Characterisation of *L. digitata*

2.3.1 Multi Element Analysis

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

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

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

2.3.2 Thermal Characterisation

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

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

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

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

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

2.3.3 Dielectric properties

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

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

2.4 Microwave pyrolysis experiments

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

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

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

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

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

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

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

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

2.5 Pyrolytic product analysis

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

3 Results and Discussion

3.1 Biochemical Characterisation

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

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

3.2 Thermal and Dielectric Characterisation

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

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

3.3 Microwave Pyrolysis Trials

3.3.1 Incident Power and Absorbed Energy

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

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

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

3.3.2 Native L. digitata Microwave Trials

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

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

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

3.3.3 L. digitata Residue Microwave Trials

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

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

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

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

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

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

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

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

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

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

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

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

4 Conclusions

Microwave pyrolysis of native *L. digitata* and its residue generated from an extraction process 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; methyl 5-oxoprolinate. 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.

Acknowledgements

This research was funded and supported through a BP plc sponsored Nottingham Summer Engineering Research Programme (N-SERP) awarded to ETK and OSAW. The authors would like to thank Dr Tamara Monti for her support and assistance with the experimental set-up.

References

1. Union, E., *Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC.* Official Journal of the European Union, 2009. **5**: p. 2009.
2. EC, *Directive (EU) 2015/1513 of the European Parliament and of the Council of 9 September 2015 amending Directive 98/70/EC relating to the quality of petrol and diesel fuels and amending Directive 2009/28/EC on the promotion of the use of energy from renewable sources*. 2015, Official Journal of the European Union: Brussels.
3. Dave, A., et al., *Techno-economic assessment of biofuel development by anaerobic digestion of European marine cold-water seaweeds.* Bioresource technology, 2013. **135**: p. 120-127.
4. Cherubini, F., *The biorefinery concept: using biomass instead of oil for producing energy and chemicals.* Energy conversion and management, 2010. **51**(7): p. 1412-1421.
5. Behera, S., et al., *Scope of algae as third generation biofuels.* Front Bioeng Biotechnol, 2014. **2**: p. 90.
6. van Hal, J.W., W. Huijgen, and A. López-Contreras, *Opportunities and challenges for seaweed in the biobased economy.* Trends in biotechnology, 2014. **32**(5): p. 231-233.
7. Adams, J., et al., *Seasonal variation in Laminaria digitata and its impact on biochemical conversion routes to biofuels.* Bioresource technology, 2011. **102**(21): p. 9976-9984.
8. Bikker, P., et al., *Biorefinery of the green seaweed Ulva lactuca to produce animal feed, chemicals and biofuels.* Journal of applied phycology, 2016. **28**(6): p. 3511-3525.
9. Baghel, R.S., et al., *Biorefining of marine macroalgal biomass for production of biofuel and commodity chemicals.* Green Chemistry, 2015. **17**(4): p. 2436-2443.
10. Yuan, Y. and D.J. Macquarrie, *Microwave assisted step-by-step process for the production of fucoidan, alginate sodium, sugars and biochar from Ascophyllum nodosum through a biorefinery concept.* Bioresource technology, 2015. **198**: p. 819-827.
11. Glasson, C.R., et al., *A cascading biorefinery process targeting sulfated polysaccharides (ulvan) from Ulva ohnoi.* Algal Research, 2017. **27**: p. 383-391.
12. Kumar, S., et al., *Bioethanol production from Gracilaria verrucosa, a red alga, in a biorefinery approach.* Bioresource technology, 2013. **135**: p. 150-156.
13. Kostas, E.T., D.A. White, and D.J. Cook, *Development of a bio-refinery process for the production of speciality chemical, biofuel and bioactive compounds from Laminaria digitata.* Algal Research, 2017. **28**: p. 211-219.
14. Trivedi, N., et al., *An integrated process for the extraction of fuel and chemicals from marine macroalgal biomass.* Scientific reports, 2016. **6**: p. 30728.
15. Kumar, S. and D. Sahoo, *A comprehensive analysis of alginate content and biochemical composition of leftover pulp from brown seaweed Sargassum wightii.* Algal Research, 2017. **23**: p. 233-239.
16. Anastas, P.T., John C. Warner, *Green chemistry: theory and practice*. 2000: Oxford university press.
17. Bharathiraja, B., et al., *Aquatic biomass (algae) as a future feed stock for bio-refineries: A review on cultivation, processing and products.* Renewable and Sustainable Energy Reviews, 2015. **47**: p. 634-653.
18. Bridgwater, A., D. Meier, and D. Radlein, *An overview of fast pyrolysis of biomass.* Organic geochemistry, 1999. **30**(12): p. 1479-1493.
19. Oasmaa, A. and S. Czernik, *Fuel oil quality of biomass pyrolysis oils state of the art for the end users.* Energy & Fuels, 1999. **13**(4): p. 914-921.
20. Vitasari, C.R., G. Meindersma, and A.B. De Haan, *Water extraction of pyrolysis oil: The first step for the recovery of renewable chemicals.* Bioresource technology, 2011. **102**(14): p. 7204-7210.

21. Robinson, J., et al., *Microwave pyrolysis of biomass: control of process parameters for high pyrolysis oil yields and enhanced oil quality.* Energy & Fuels, 2015. **29**(3): p. 1701-1709.
22. Budarin, V.L., et al., *Microwave-mediated pyrolysis of macro-algae.* Green Chemistry, 2011. **13**(9): p. 2330-2333.
23. Ferrera-Lorenzo, N., et al., *Conventional and microwave pyrolysis of a macroalgae waste from the Agar–Agar industry. Prospects for bio-fuel production.* Bioresource technology, 2014. **151**: p. 199-206.
24. Hong, Y., et al., *Microwave-enhanced pyrolysis of macroalgae and microalgae for syngas production.* Bioresource Technology, 2017. **237**: p. 47-56.
25. Bermúdez, J.M., et al., *Microwave-induced low temperature pyrolysis of macroalgae for unprecedented hydrogen-enriched syngas production.* RSC Advances, 2014. **4**(72): p. 38144-38151.
26. Kostas, E.T., D. Beneroso, and J.P. Robinson, *The application of microwave heating in bioenergy: A review on the microwave pre-treatment and upgrading technologies for biomass.* Renewable and Sustainable Energy Reviews, 2017. **77**: p. 12-27.
27. Watts, M. and C. Mitchell, *A pilot study on iodine in soils of Greater Kabul and Nangarhar provinces of Afghanistan.* Environmental geochemistry and health, 2009. **31**(4): p. 503-509.
28. Lester, E., M. Gong, and A. Thompson, *A method for source apportionment in biomass/coal blends using thermogravimetric analysis.* Journal of analytical and applied pyrolysis, 2007. **80**(1): p. 111-117.
29. ISO, N. *Solid mineral fuels-Determination of gross calorific value by the bomb calorimetric method, and calculation of net calorific value*. 2004. ICS.
30. Adam, M., et al., *Microwave fluidized bed for biomass pyrolysis. Part I: Process design.* Biofuels, Bioproducts and Biorefining, 2017. **11**(4): p. 601-612.
31. Robinson, J., et al., *Understanding microwave heating effects in single mode type cavities-theory and experiment.* Physical Chemistry Chemical Physics, 2010. **12**(18): p. 4750-4758.
32. Ogunniran, O., et al., *Enhancing evaporative mass transfer and steam stripping using microwave heating.* Chemical Engineering Science, 2017. **165**: p. 147-153.
33. Pert, E., et al., *Temperature measurements during microwave processing: the significance of thermocouple effects.* Journal of the American Ceramic Society, 2001. **84**(9): p. 1981-1986.
34. Mazubert, A., et al., *Key role of temperature monitoring in interpretation of microwave effect on transesterification and esterification reactions for biodiesel production.* Bioresour Technol, 2014. **161**: p. 270-9.
35. Hashim, M. and K. Chu, *Biosorption of cadmium by brown, green, and red seaweeds.* Chemical Engineering Journal, 2004. **97**(2-3): p. 249-255.
36. Wang, N., et al., *A comparative study of microwave-induced pyrolysis of lignocellulosic and algal biomass.* Bioresource technology, 2015. **190**: p. 89-96.
37. Beneroso, D., et al., *Microwave pyrolysis of microalgae for high syngas production.* Bioresource Technology, 2013. **144**: p. 240-246.
38. Debalina, B., R.B. Reddy, and R. Vinu, *Production of carbon nanostructures in biochar, bio-oil and gases from bagasse via microwave assisted pyrolysis using Fe and Co as susceptors.* Journal of analytical and applied pyrolysis, 2017. **124**: p. 310-318.
39. Klinger, J.L., et al., *Effect of biomass type, heating rate, and sample size on microwave-enhanced fast pyrolysis product yields and qualities.* Applied Energy, 2018. **228**: p. 535-545.
40. Jimenez, G.D., et al., *New insights into microwave pyrolysis of biomass: Preparation of carbon-based products from pecan nutshells and their application in wastewater treatment.* Journal of Analytical and Applied Pyrolysis, 2017. **124**: p. 113-121.
41. Meredith, R.J., *Engineers' handbook of industrial microwave heating*. 1998: Iet.
42. Bridgwater, A.V., *Review of fast pyrolysis of biomass and product upgrading.* Biomass and bioenergy, 2012. **38**: p. 68-94.

43. Wang, S., et al., *Study of pyrolytic mechanisms of seaweed based on different components (soluble polysaccharides, proteins, and ash).* Journal of Renewable and Sustainable Energy, 2017. **9**(2): p. 023102.
44. Beneroso, D., et al., *Microwave pyrolysis of biomass for bio-oil production: Scalable processing concepts.* Chemical Engineering Journal, 2017. **316**: p. 481-498.
45. Adam, M., et al., *Microwave fluidized bed for biomass pyrolysis. Part II: Effect of process parameters.* Biofuels, Bioproducts and Biorefining, 2017. **11**(4): p. 613-624.
46. Mazubert, A., et al., *Key role of temperature monitoring in interpretation of microwave effect on transesterification and esterification reactions for biodiesel production.* Bioresource technology, 2014. **161**: p. 270-279.
47. Metaxas, A.a. and R.J. Meredith, *Industrial microwave heating*. 1983: IET.
48. Dai, L., et al., *Hydrothermal pretreatment of bamboo sawdust using microwave irradiation.* Bioresource technology, 2018. 247: p. 234-241.
49. Kim, J.-S., *Production, separation and applications of phenolic-rich bio-oil–a review.* Bioresource technology, 2015. **178**: p. 90-98.
50. Ross, A., et al., *Investigation of the pyrolysis behaviour of brown algae before and after pre-treatment using PY-GC/MS and TGA.* Journal of Analytical and Applied Pyrolysis, 2009. **85**(1-2): p. 3-10.
51. Adams, J., et al., *Seasonal variation in the chemical composition of the bioenergy feedstock Laminaria digitata for thermochemical conversion.* Bioresource technology, 2011. **102**(1): p. 226-234.
52. Membere, E. and P. Sallis, *Thermochemical characterization of brown seaweed, Laminaria digitata from UK shores.* Journal of Analytical and Applied Pyrolysis, 2018. **131**: p. 42-51.
53. Shekhar, S.H., et al., *Brown seaweed species from Strangford Lough: compositional analyses of seaweed species and biostimulant formulations by rapid instrumental methods.* Journal of applied phycology, 2012. **24**(5): p. 1141-1157.
54. Anastasakis, K., A. Ross, and J. Jones, *Pyrolysis behaviour of the main carbohydrates of brown macro-algae.* Fuel, 2011. **90**(2): p. 598-607.
55. Kebelmann, K., et al., *Thermo-chemical behaviour and chemical product formation from Polar seaweeds during intermediate pyrolysis.* Journal of analytical and applied pyrolysis, 2013. **104**: p. 131-138.
56. Shepherd, B., et al., *Microwave pyrolysis of biomass within a liquid medium.* Journal of analytical and applied pyrolysis, 2018. **134**: p. 381-388.