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Microwave-mediated pyrolysis of macro-algae†

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Macro-algae (seaweed) is an abundant and, for the most part, under-utilised resource. This study has shown that microwave (MW)-mediated pyrolysis of seaweed occurs at extremely low temperatures and produces chemical rich bio-oils which are rich in aromatics, sugars and other high value chemicals.

Biomass is an up and coming resource for biofuels and valuable chemical production, preferable to fossil fuel as carbon dioxide is maintained within a continuous closed loop.^{1,2} However, growing bioenergy markets derived from terrestrial biomass could increase competition for land and lead to higher food prices.³ Marine biomass could be a promising alternative making up 50% of global biomass.^{4–6} Cultivating seaweeds helps ocean remediation, decreases eutrophication and red tide microalgae,⁷ and has a beneficial effect on the wider sea environment by releasing iodine, a key part of the water cycle and global cooling.⁸ Seaweed has one of the highest solar energy conversion⁹ and CO₂ capture efficiencies with 460 million tons of carbon adsorbed annually¹⁰ which equates to in excess of 10 billion tonnes of seaweed per year. Also, macro-algae is opposite to micro-algae, being easily harvested from water and only containing approximately 7–10% moisture making it suitable for thermal treatment. It is currently problematic to utilise this huge quantity of macro-algae effectively. Seaweeds can be used in multiple commercial applications including food, medicine, and fertiliser (Table 1). Currently less than 1% of available seaweed is utilised, and if these rich seaweed resources were to be sustainably and efficiently exploited for fuel and chemicals, they would contribute significantly to fossil fuel replacement.¹¹ Macro-algae integration into a biorefinery is a challenge as it contains significantly increased levels of halogenated compounds, alkali earth and heavy metals, in comparison to terrestrial lignocellulosic biomass, restricting its use in direct combustion.^{12,13} Furthermore, seaweed is not easily used under typical fermentation or anaerobic digestion conditions requiring specialist enzymes and conditions for conversion.¹⁴

Table 1 Commercial market for seaweed products²²

Industry	Market value/\$ ^a	Quantity/tonnes ^b
Food (human)	6 bn	6.4 m
Hydrocolloids (inc. medical uses)	(0.702 bn)	(~0.9 m)
Agar	255.6 m	55 650 ^c
Alginate	158.4 m	126 500 ^c
Carrageenan	288 m	33 000 ^c
Feed (animal)	6 m	50 000
Fertilizer	6 m	10 000
Total	6.6–7.2 bn	7.5–8 m

^a Adjusted to current market value. ^b Wet seaweed harvested. ^c Dry basis.

Of the in excess of 3000 papers published on seaweed, only two investigate pyrolysis.^{11,15} Pyrolysis is an established technique for deconstructing biomass using thermal energy under inert atmospheres into high value products such as platform molecules for synthesis, bio-oils for fuel and bio-chars for energy.¹⁶ Over recent years microwave-mediated pyrolysis of polymers,¹⁷ coal¹⁸ and biomass^{19–21} has proved to be an effective modification of this technology producing different product streams due to time savings, environmental benefits and increased process selectivity.^{23–25} Microwave heating has been shown to often be more energy-efficient than conventional heating²⁶ and industrial scale microwave reactors for continuous flow manufacturing processes are now available.²⁷ In this study we propose to investigate microwave interaction with macro-algae and potential for generation of pyrolysis products. Microwave-mediated pyrolysis experiments with *Gracilaria* macro-algae‡ showed that decomposition occurred at very low temperatures (close to 130 °C) (Fig. 1) which is lower than the microwave-mediated pyrolysis of cellulose (~180 °C) and over 130° lower than conventional pyrolysis (Fig. 2).²⁰ During pyrolysis a large volume of gas (up to 320 cm³ g⁻¹ measured at 25 °C) is evolved, with a rate of evolution in excess of 800 cm³ s⁻¹ g⁻¹ (Fig. 1 and Film 1S†). It was observed that gas and bio-oil formation are proportional to each other, and therefore the volume of gas was used as a measurement of pyrolysis rate. Measurement of temperature is a key issue.²⁸ Within the microwave cavity bulk temperature cannot be directly measured as the temperature probe will heat at a different rate to the substrate under investigation and external measurement systems suffer from lag due to thermal gradients within the sample. There is a considerable but predictable

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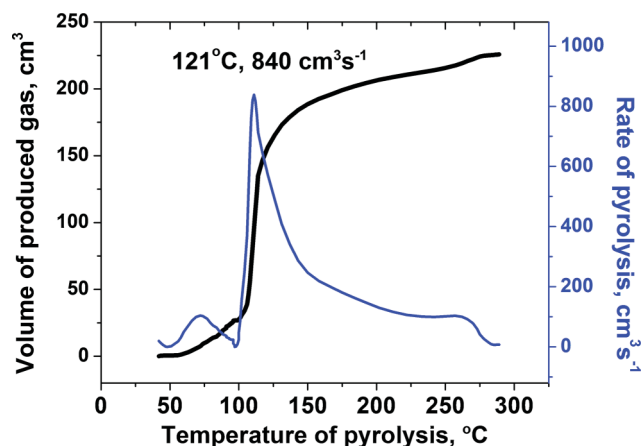


Fig. 1 Gas evolution as a function of time for microwave pyrolysis of macro-algae per gram of algae. Microwave power – 200 W, sample mass – 0.7 g, open vessel.

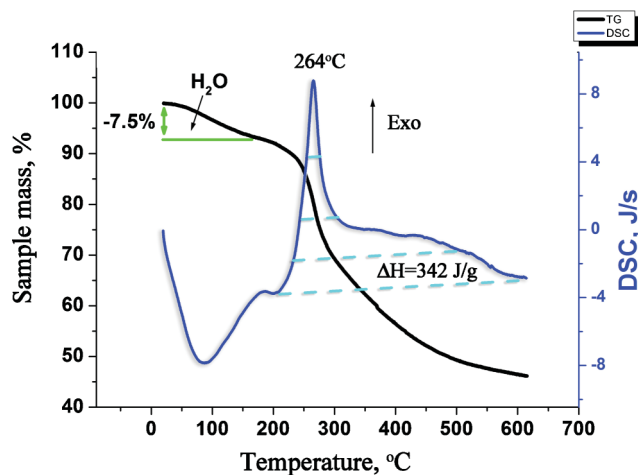


Fig. 2 STA profile of macro-algae thermal pyrolysis.

difference between internal fibre-optic and external infra-red probes using inorganic oxide samples.²⁹ The latter technique showed a 5–50 °C increase in the internal measurement which was believed to be caused by hot spots. However, we have found when pyrolysing seaweed that there is little difference between the two measurement sources at temperatures below 100 °C; at higher temperatures the variance ranged from 4 K at 100 °C to 12 K at 170 °C. This difference in behaviour of inorganic oxide and seaweed could be explained by the fact that at low temperature physisorbed water vapour aided thermal conduction and allows an even temperature distribution through the sample. At higher temperatures when pyrolysis occurs, evolved volatiles cool the hot spot by evaporation and again distribute the heat more evenly.

Both the fibre optic and the infra-red measurement are separated from the biomass by glass. To avoid any effects from insulation a novel direct contact experiment was developed. A non-microwave-absorbing polypropylene polymer bead (20 mg) was mixed with seaweed (440 mg) and then irradiated with microwaves (300 W) to a set temperature, as measured by the infra-red probe. The bead was removed and the extent of melting examined; Fig. 3 shows beads heated by both microwave

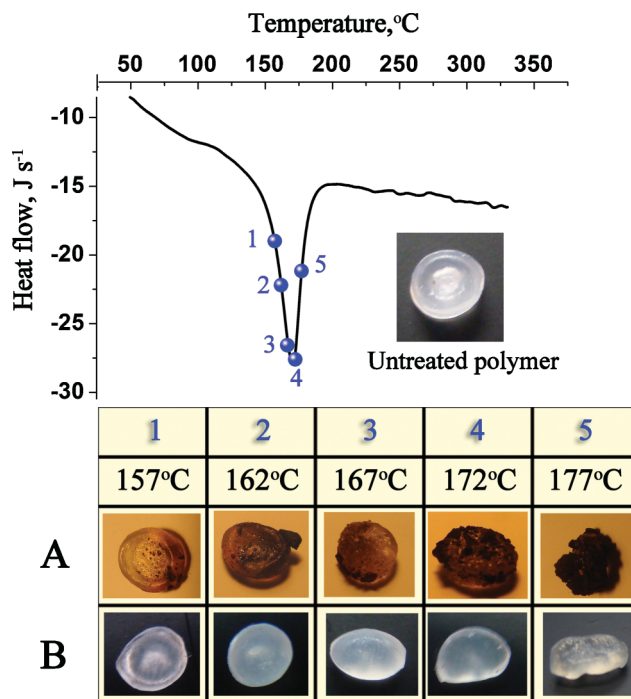


Fig. 3 Photographs and melting point of polypropylene (mp. 172 °C) at a range of temperatures. A: inside microwave cavity and B: under conventional heating.

(A) and conventional heating (B). Similar deformation is observed for both heating methods approaching the melting point, which correlated with the DSC profile for the melting of the polymer. Above the melting point complete melting of the bead is observed (177 °C). This data suggests that the sample surface temperature, measured by IR probe, is within 5 °C of the sample core temperature, thus confirming the low pyrolysis temperature.

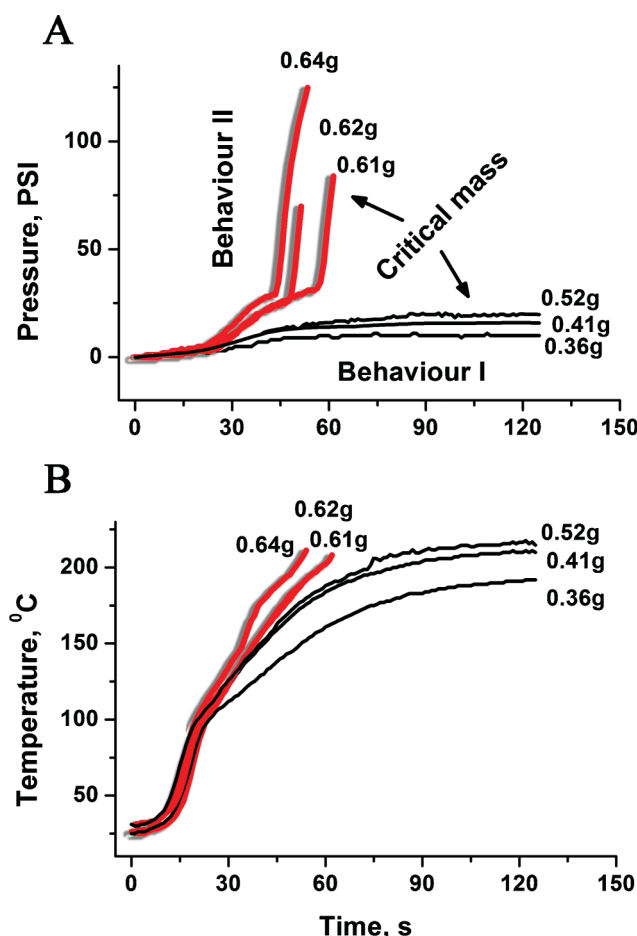
The investigation then turned to studying bio-oil composition and maximising bio-oil yield. In our initial experiments the heating rate was relatively low at ~90 K min⁻¹. The link between high bio-oil yield and high heating rate is known;³⁰ in conventional pyrolysis heating rates exceed 600–60,000 K min⁻¹. Parameters to increase heating rate include using polar compounds such as water, increasing mass and size of the sample which subsequently increase efficiency of microwave absorption. Water is a strong microwave absorber, which when present increases the rate of heating and therefore bio-oil yield. Samples with between 0 and 15% initial water content were heated under microwave conditions. As can be seen in entries 1–6 of Table 2, poor oil yields were observed with dried samples. However, oil yield plateaued at ~10% bio-oil with over 7% initial water content. Increasing power input for a given mass of sample was found to give little increase in oil yield.

Mass proved to have a significant influence on pyrolysis behaviour, small changes in sample mass lead to large changes in oil yield from 12% increasing to 16.1% for 200 W and from 8.5% increasing to 13.6% for 300 W (Table 2 entries 9–12 and 13–16). Fig. 4A shows this effect on rate of pyrolysis (measured gas evolution as pressure change in a closed vessel); it can be seen that two pyrolysis behaviours exist. At low sample masses (<0.52 g) a “slow” pyrolysis (type I) behaviour occurs

Table 2 Influence of process parameters on bio-oil and char yield

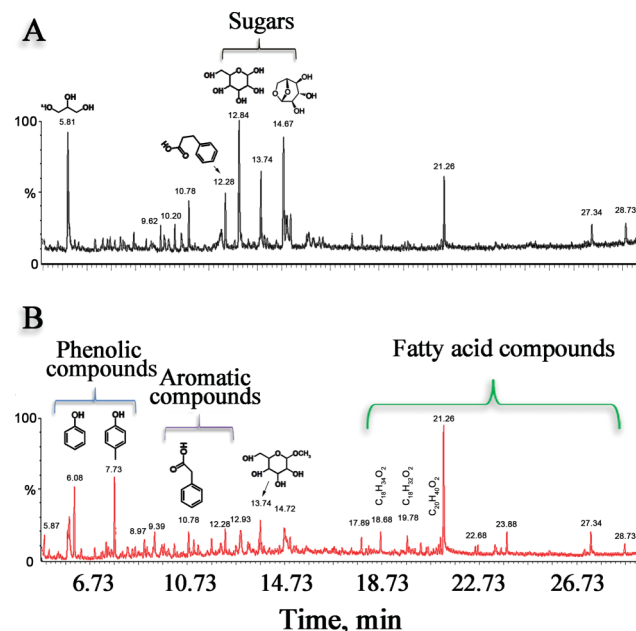
N	Sample mass (g)	Power (W)	Initial Water (%) ^a	Product yield (%)	
				Bio-Oil ^b	Char
1	0.5	200	0	2.9	62.1
2	0.5	200	0	3.4	71.0
3	0.5	200	7.0	10.5	52.3
4	0.5	200	11.5	9.4	54.1
5	0.5	200	15.8	9.5	54.2
6	0.21	200	7.5	10.7	64.0
7	0.36	200	7.5	11.2	58.1
8	0.41	200	7.5	11.5	54.6
9	0.5	200	7.5	12	47.1
10	0.57	200	7.5	12.4	40.3
11	0.61	200	7.5	16.1	33.4
12	0.64	200	7.5	15.7	32.2
13	0.214	300	7.5	8.5	58.3
14	0.244	300	7.5	9.7	55.3
15	0.299	300	7.5	13.6	53.5
16	0.369	300	7.5	13.3	40.7

^a Water content of native seaweed is 7.5% as received. ^b Bio-oil contains less than 1% water, water is fractionated *in situ*.

**Fig. 4** Influence of initial sample mass on microwave pyrolysis kinetic profile measured by A: pressure, and B: temperature.

characterised by low gas and bio-oil evolution, with higher char yield. In these conditions gas yield is linear with initial sample mass; in contrast, small changes in sample mass between 0.52 g and 0.61 g gives large changes in final gas volume released (final

gas pressure rising from 0.15 to 0.5 MPa), type II behaviour. Fig. 4B shows a significant difference between the rate of heating within the sample for type I and II processes. The “fast” type II heating rate remains high throughout the pyrolysis process indicating an auto-catalytic mechanism with maximum heating rate close to 400 K min⁻¹. This can be explained due to the difference between the activation energy of decomposition and diffusion. At higher heating rates the rate of volatile production exceeds the rate at which the volatiles can diffuse from the biomass leading to a concentration build-up. Microwave pyrolysis studies by Kreiger indicated the importance of polar volatile compounds in the initiation of pyrolysis as a good absorber of microwave irradiation.³¹ Furthermore, these volatiles are acidic which further helps catalyse the exothermic decomposition (see Fig. 2) of biomass and hence volatile production. GC-MS analysis of bio-oils showed that product mixture varied greatly with microwave-mediated pyrolysis conditions. Fig. 5 shows the chromatograms for bio-oil obtained under the two differing behaviours. Chromatogram A shows oils produced by type I behaviour (low sample mass) with the major products being fermentable anhydro-sugars such as levoglucosan (reaction time 14.8 min). Functionalised fermentable sugars are of great interest as they are suitable for use as platform molecules in the synthesis or in the generation of bio-ethanol and citric acid *via* fermentation.^{32,33}

**Fig. 5** GC-MS spectra for microwave-derived bio-oils from seaweed. A: bio-oil derived from type I behaviour; B: bio-oil derived from type II behaviour.

In contrast, Fig. 5B shows the composition of bio-oil derived with high sample mass demonstrating type II pyrolysis behaviour, rapid heating rates and high gas evolution. Whilst the functionalised sugars are still present, the major products are phenol (reaction time 6.1 mins) and 4-methyl phenol (reaction time 7.73 mins). The presence of aromatic and phenolic compounds from low-lignin biomass indicates a non-direct source of these chemicals. Fatty acids and fatty acid type compounds observed (reaction time >17.89 mins) are present from direct

microwave enhanced extraction of the seaweed and not as a result of pyrolysis decomposition. To ensure that the majority of the products were being seen by the GC-MS, it was found that 80% of the bio-oil was volatile below 250 °C using TG-IR analysis.

Yield of oil obtained during microwave pyrolysis at the higher sample mass conditions is ~21% as percentage of the organic material in seaweed. This is significantly higher than 14.2% of oil yield obtained with conventional pyrolysis at a temperature of 800 °C.¹⁵ Microwave derived bio-oil show suitable properties as a potential bio-fuel: calorific value 22.1 kJ g⁻¹; water and ash contents 2.2 and 4.7% respectively; pH is greater than 2.8. Calorific value of bio-char obtained in the same experiment is 16.2 kJ g⁻¹.

Water remediation *Gracilaria* macro-algae used in Foggia, Italy to capture high nitrogen agricultural runoff to an inland lagoon, was used for this initial study. Following these initial observations two differently sourced macro-algae were screened: a) *Laminara Digitata*, a whole seaweed from the west coast of Scotland, used without treatment; b) Shetland coastal seaweed (*Ascophyllum Nodosum*) used following extraction. This range was chosen to reflect possible available macro-algae biomass - a natural unmodified, a post-extraction and macro-algae used for water remediation. Behaviour of all three materials was found to be similar, all under going pyrolysis at extremely low temperatures (130 °C).

Conclusions

In this work we have investigated the behaviour of seaweed, an under-utilised and abundant biomass resource under microwave pyrolysis conditions. It was discovered that seaweed undergoes pyrolysis at extremely low temperatures around 130 °C, less than conventional biomass and around 400 K lower than flash pyrolysis. Bio-oil and char were formed as products of the microwave-mediated pyrolysis. Through small adjustments in mass of sample it was observed that vastly different reaction pathways occur—one a “slow” pyrolysis signified by low heating rates, low gas evolution and an anhydro-sugar rich bio-oil with high char yield. Conversely at higher sample masses rapid gas evolution and high heating rates (up to 400 K min⁻¹) were observed, with higher bio-oil yields (up to 21% from organic matter of seaweed) which are rich in phenolic and fatty acid compounds, and bio-char suitable for domestic use. This yield is significantly higher than obtained from conventional heating, 14%.

This information will be critically important for design of an industrial scale microwave processor, ready for generation of higher value chemicals available from non-food biomasses. Low temperature and high rate of decomposition, significant yield of bio-oil and flexibility of microwave pyrolysis conditions make it very attractive as part of a seaweed biorefinery.

Notes and references

† Typical experimental conditions: powdered seaweed samples were weighed and densely packed into a 10 mL microwave tube, sealed using the microwave tube lid, placed into a CEM Discover laboratory (mono-mode 0–300 W) microwave reactor and irradiated under varying conditions, typically a power of 100–300 W and a temperature ranging

from 100 to 300 °C. Following irradiation, solids were washed with ~10 mL methanol, the resultant liquid and solid were dried *in vacuo*, weighed and analysed using standard methodology. *Gracilaria* samples were obtained from the Lesina lagoon, Foggia, Italy (ash and water content 21% and 7.5%, respectively). *Laminara Digitata* samples (ash and water content 17.1% and 7.2%, respectively) were collected from the West Coast of Scotland. *Ascophyllum Nodosum* samples (ash and water content 14.5% and 6.2% correspondingly) were supplied by Bod Ayre Products, Shetland Isles, United Kingdom.

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