Classification of macroalgae as fuel and its thermochemical behaviour

A.B. Ross [*], J.M. Jones, M.L. Kubacki, T. Bridgeman

Energy and Resources Research Institute, School of Process, Environmental and Materials Engineering, University of Leeds, Woodhouse Lane, Leeds LS29JT, UK

Abstract

A preliminary classification of five macroalgae from the British Isles; *Fucus vesiculosus, Chorda filum, Laminaria digitata, Fucus serratus, Laminaria hyperborea,* and *Macrocystis pyrifera* from South America, has been presented in terms of a Van Krevelen diagram. The macroalgae have been characterised for proximate and ultimate analysis, inorganic content, and calorific value. The different options for thermal conversion and behaviour under combustion and pyrolysis have been evaluated and compared to several types of terrestrial biomass including *Miscanthus*, short rotation Willow coppice and Oat straw. Thermal treatment of the macroalgae has been investigated using thermogravimetry (TGA) and pyrolysis-gc-ms. Combustion behaviour is investigated using TGA in an oxidising atmosphere. The suitability of macroalgae for the different thermal processing routes is discussed. Ash chemistry restricts the use of macroalgae for direct combustion and gasification. Pyrolysis produces a range of pentosans and a significant proportion of nitrogen containing compounds. High char yields are produced.
© 2007 Elsevier Ltd. All rights reserved.

Keywords: Combustion; Fuel analysis; Macroalgae; Marine biomass; Pyrolysis

1. Introduction

The focus on the use of biomass as an alternative feedstock to fossil fuels is intensifying due to its role in reducing CO_2 emissions. Currently many technologies are under investigation for utilisation of biomass both for power generation and for production of bio-oil for transportation and chemical commodities. Two of the main issues of biomass utilisation are security of supply and the development of an infrastructure capable of maintaining the supply of biomass of sufficient quality. There is now a growing body of research into the farming of energy crops, especially since current legislation in the UK necessitates the use of such energy crops in order to qualify for "renewable obligation credits", an important mechanism for increasing the penetration of biomass utilisation in the energy sector. Despite this, there are still concerns that the amount of biomass required in order to make a significant impact on CO_2 reduction will be governed by supply. As a consequence there is interest in alternative biomass resources including biomass from an aquatic environment.

Marine macroalgae is one such source of aquatic biomass and potentially represents a significant source of renewable energy. The average photosynthetic efficiency of aquatic biomass is 6–8% (Renewable biological systems for alternative sustainable energy production, 1997) which is much higher than that of terrestrial biomass (1.8–2.2%). Either microalgae or marine macroalgae (kelp or seaweed) could be used for solar energy conversion and biofuel production.

Macroalgae are fast growing marine and freshwater plants that can grow to considerable size (up to 60 m in length). Growth rates of marine macroalgae far exceed those of terrestrial biomass, mainly due to no water limitations (Gellenbeck and Chapman, 1983). Annual primary production rates (grams $C\,m^{-2}\,yr^{-1}$) are higher for the major marine macroalgae than for most terrestrial biomass. Macroalgae can be subdivided into the blue algae (Cyanophyta), green algae (Chlorophyta), brown algae (Phaeophyta) and the red algae (Rhodophyta). The uses

---

[*] Corresponding author. Tel.: +44 113 343 2459; fax: +44 113 246 7310
  E-mail address: a.b.ross@leeds.ac.uk (A.B. Ross).

of seaweeds at present are as human foods, cosmetics, fertilizers, and for the extraction of industrial gums (phytocolloids) and chemicals (Abbott, 1982). They have the potential to be used as a source of long- and short-chain chemicals with medicinal and industrial uses (Abbott, 1982). Significant amount of seaweeds are used as foods in Asia, although this is limited in Europe. Seaweeds are cultured on a massive scale in the far East, and on a smaller scale in Europe. Clearly where the end product is a high value food or hydrocolloid, it is economically viable to culture seaweeds. Seaweeds are the main resource materials for phytocolloids such as agar, carrageenan (derived from Rhodophyta) and alginates (derived from Phaeophyta) (Abbott, 1982; Cadée, 1992). The residues from such processing also represent a renewable source of energy.

Previous studies into farming of marine biomass for energy purposes has shown difficulties (Wise, 1981) particularly for off shore kelp farming. However, since then, the farming practices have improved significantly. The challenge includes the feasibility of growing fast rate macroalgae in the open ocean, cutting costs of collection and avoiding environmental damage. If farming methods were improved, marine biomass could become a potentially viable energy crop. Inshore seaweed aquaculture is well established and has less challenges.

Kelp are large seaweeds, belonging to the brown algae and classified in the order Laminariales. Certain kelp varieties are capable of producing considerable amounts of biomass such as *Macrocystis pyrifera* (giant bladder kelp) which grows of the coast of Chile, and North America and *Laminaria japonica* (kombu) which grows off the coast of East Asia. The kelp farming industry around the British Isles is relatively small but significant quantities of kelp beds exist around the west coast of Ireland and Scotland in quantities sufficient for exploitation. The kelp species around the UK are smaller (up to 3 m in length), and the main species include *Laminaria digitata* (Oarweed; Tangle), *Laminaria hyperborea* (Curvie), *Laminaria ochroleuca* (Bachelot de la Pylaie) and *Laminaria saccharina* (Sugarwack).

Much of the existing research in energy and fuels from algae has been devoted towards biodegradation, methane production and biodiesel production from microalgae (Scragg et al., 2002. Sawayama, 1999; Miao et al., 2004; Minowa et al., 1994; Wise, 1981). A number of studies have investigated bio-degradation of macroalgae for biogas production (Wise, 1981; Song et al., 2006; Chynoweth et al., 2001). Anaerobic digestion of marine macroalgae has been demonstrated with both high yields and conversion rates, although suitable conditions vary amongst different species and within the same species at different points in the growth cycle (Chynoweth et al., 1993). Early studies suggest biogas production from macroalgae would be more expensive than terrestrial biomass (Wise, 1981). The major limitation of anaerobic digestion is that it is usually incomplete and process rates are significantly slower than those of thermal processes.

Less attention has been devoted to thermochemical conversion of kelp. The different thermochemical options for macroalgae utilisation include direct combustion, gasification, pyrolysis and liquefaction. Some preliminary studies of thermal behaviour have been made (Ross and Jones, 2005; Wang et al., 2006). Combustion and co-firing characteristics are yet to be evaluated to a wide extent. A number of studies have identified the potential of aquatic biomass in carbon capture schemes (Raiko et al., 2003; Tarwadi and Chauhan, 1987; Brown and Zeiler, 1993). Strategies have been envisaged of combustion followed by the CO_2 produced being fed into the growth chambers to form a closed fuel cycle (Aresta et al., 2005), this has similarly been proposed for microalgae (Maeda et al., 1995). Methane can also be produced from wet biomass by thermal gasification. Thermal processes require feeds with low water content (<50%) or feeds capable of being dewatered by mechanical means, the exception being liquefaction in superheated water which can tolerate high moisture content feedstocks.

The biochemical composition of different seaweed species have been studied in detail (McHugh, 2003; Sánchez-Machado et al., 2004) and the seasonal variations in bio-composition and ash content is well documented (Marinho-Soriano et al., 2006). However, there is less information describing the fuel properties and there have been few studies comparing the composition of marine biomass to conventional terrestrial biomass. The present study has determined the fuel properties of a number of macroalgae including *L. digitata* (Oarweed; Tangle), *L. hyperborea* (Curvie), *L. saccharina* (Sugarwack), *Fucus vesiculous* (Bladder Wrack), *Fucus serratus* (Saw Wrack) *Chorda filum* (Chord weed), and *M. pyrifera* (Giant kelp). The suitability of macroalgae for energy and fuel production is discussed in terms of the different thermochemical routes. The compositions of the macroalgae are compared to well characterised energy crops currently under investigation for power generation in the UK. Preliminary classification of macroalgae, has been presented in terms of a Van Krevelen diagram. The combustion properties are determined using thermogravimetry (TGA) in an oxidising atmosphere using previously developed methods (Jones, 2004). The production of liquid fuels and chemical commodities have been investigated by flash pyrolysis using py-gc-ms. The inorganic contents of the macroalgae have been characterised and the influence of this inorganic matter and its limitations for thermal processing is discussed. The difference in terms of polymeric organic material and the significance of this on the products from pyrolysis is also discussed.

2. Experimental

2.1. Sample preparation and analysis

Samples of seaweed were collected, water washed in distilled water and air-dried. The dry material was ground and sieved to a particle size of <90 μm before analysis in a grinder. This preliminary study has used both seaweed litter (recently deposited thus subject to minimal decomposition) and a sample of giant kelp from South America (*M. pyrif-*

era). The seaweed litter collected from the Cornish coast on the south coast of England (February, 2005) and include a number of different genera of brown seaweed including *L. digitata*, *L. hyperborea*, *F. vesiculous*, *F. serratus* and *C. filum*. A sample of *M. pyrifera* was supplied by the Irish Seaweed Centre. The terrestrial energy crops used for comparison include *Miscanthus*, Oat straw and short rotation Willow coppice.

2.1.1. Proximate and ultimate analysis

Moisture analyses were carried out in accordance to standard CEN/TS 14774-3:2004 by drying the samples in a Carbolite MFS Oven in the presence of nitrogen until constant weight was achieved. The ash contents were obtained following standard DD CEN/TS 14775:2004 after low temperature oxidation (550 °C) of the samples in a Carbolite OAF 10/1 furnace. The volatile content was determined by a TGA method, as outlined in the next section. Finally, the fixed carbon content was calculated by difference. The ash contents proved to be variable and this is highlighted later. The C, H, N, O, S contents in the biomass were measured using a CE Instruments Flash EA 1112 Series elemental analyser. All measurements were repeated in triplicate and a mean value is reported. Chlorine, bromine and iodine were determined as total halogens by Schoniger flask combustion and titration with mercuric nitrate.

2.1.2. Calorific value determination

Calorific values (CV) were measured in duplicate using a Gallenkamp Adiabatic Bomb Calorimeter with its Autocell controller and following BS1016 part 5 (1977). The sample was oxidised by combustion in an adiabatic bomb containing oxygen under pressure. The heat of combustion was determined by measuring the temperature rise of a known mass of water. The dissolved sulphate was calculated during this measurement (by titration) so that the calorific value was corrected for this contribution.

2.1.3. Metal analysis

The samples were wet digested in HNO_3 and HF in a closed vessel. The solution was analysed for metals by inductively coupled plasma spectrometry (ICP) with mass spectrometric detection. This method allows total silica to be measured and is more accurate for trace volatile metals such as As and Se.

2.1.4. Analytical pyrolysis and thermal analysis

Pyrolysis-gc-ms analysis was performed on a CDS 5000 series pyrolyser connected to a Shimadzu 2010 GC–MS. Samples of 2 mg were pyrolysed at 500 °C at a ramp rate of 20 °C per milli second with a hold time of 20 s. The products were separated on an Rtx 1701 60 m capillary column, 0.25 i.d., 0.25 uf film thickness, using a temperature program of 40 °C, hold time 2 min, ramped to 250 °C, hold time 30 min, column head pressure at 40 °C of 30 psi.

Differential thermal analysis was performed in either nitrogen or air using a Stanton Redcroft DTA. Approximately 5 mg of sample was heated from 40 °C to 950 °C at a ramp rate of 25 °C min in nitrogen and air at a flow rate of 50 ml/min.

Volatile content was measured by the mass loss between 110 °C and 550 °C, fixed carbon was determined from the mass loss upon addition of air at 550 °C and ash content was determined by the mass remaining upon addition of air.

3. Results and discussion

3.1. Characterisation and classification of macroalgae

The main species of Brown seaweed used in this study are listed in Table 1 together with a summary of the fuel characteristics of proximate analysis, ultimate analysis and calorific value, in comparison, to some terrestrial energy crops. Similarly the metal contents are given in Table 2. The ultimate analyses of the macroalgae, as received, indicates that they are lower in C, H, and O than

Table 1
Macroalgae fuel analysis (as received)

| Material | Proximate (as received) by TGA and British Standard methods | | | | | HHV (ar) | Ultimate (as received) | | | | | | | |
	V.M.[a]	Fixed carbon[a]	Ash[a]	H_2O B.S.	Ash B.S.	MJ kg^{-1}	C	H	O	N	S	Total halogen mol/g	H/C	O/C
Fucus vesiculosus	51.4	23.8	11.8	12.3	22.82	15.00	32.88	4.77	35.63	2.53	2.44	11.0	1.24	0.56
Chorda filum	52.2	24.9	9.9	13.1	11.61	15.55	39.14	4.69	37.23	1.42	1.62	2.34	0.99	0.49
Laminaria digitata	53.4	25.3	10.0	13.7	25.75	17.60	31.59	4.85	34.16	0.90	2.44	2.67	1.26	0.52
Fucus serratus	45.5	24.2	18.6	11.4	23.36	16.66	33.5	4.78	34.44	2.39	1.31	0.5	1.26	0.54
Laminaria hyperborea	53.5	21.5	11.2	12.4	17.97	16.54	34.97	5.31	35.09	1.12	2.06	3.78	1.35	0.52
Macrocystis pyrifera	42.4	33.4	18.5	8.0	38.35	16.00	27.3	4.08	34.8	2.03	1.89	5.17	1.40	0.76
												wt% Cl		
Oat straw	64.9	16.9	6.7	3.9	9.4	17.80	42.75	5.22	38.71	1.06	<0.2	1.03	1.34	0.62
Miscanthus	74.2	14.1	2.1	1.9	10.9	19.08	46.32	5.58	41.79	0.56	<0.2	0.3	1.44	0.65
Willow coppice	67.5	19.1	3.0	5.3	5.9	17.69	52.69	5.92	41.90	0.48	<0.2	<0.3	1.21	0.53

B.S. Determined by British standard method for biomass at 550 °C.
[a] Determined by thermal gravimetric analysis.

terrestrial biomass and higher in N and S. There is expected to be seasonal variation as with terrestrial biomass although this is not directly addressed in this study. In general, as the seaweed moves through its growth cycle, the biochemical composition changes. In March, the macroalgae are usually high in protein, alginic acid and low in carbohydrate. During the spring as photosynthesis increases, so does the sugar content (e.g. mannitol) and there is a corresponding decrease in ash, proteins and alginic acid (Marinho-Soriano et al., 2006). On a dry ash free basis, the C, H, and O content is similar to terrestrial biomass, and Fig. 1 indicates the classification of macroalgae based on a Van Krevelen diagram (plot of H/C versus O/C atomic ratios on a dry ash free basis (daf). The macroalgae fall across the range of atomic ratios seen for other terrestrial biomass and cellulose, and are expected to have similar gross properties. However, they are chemically different as described later.

The moisture content, once air-dried, can be reduced to levels acceptable for thermal processing. Despite this the heating value is significantly lower than that of the terrestrial energy crops (cf. 14–16 MJ kg^{-1} to 17–20 MJ kg^{-1}), and in general the ash content is higher. Consequently, the metal contents are, for the most part, higher in seaweed compared to the terrestrial biomass. Total halogens vary widely from sample to sample and range from 0.5% to as high as 11%, significantly higher than terrestrial biomass (1–1.5%). In addition, macroalgae contain bromine and iodine whereas in terrestrial biomass it is predominantly chlorine.

The organic constituents in macroalgae also differ chemically to terrestrial biomass and this impacts their thermal behaviour. Kelp does not contain the same ligno–cellulosic structure as terrestrial biomass. It is usually characterised by its protein, carbohydrate, simple lipids and glycolipid content. The chemical composition of macroalgae shows variation according to species, seasons and habitats (Rupérez, 2002). The fatty acids of seaweeds are complex but generally have linear chains, an even number of carbon atoms, and one or more double bonds. The carbohydrates fraction can be sub-divided into its free sugars including
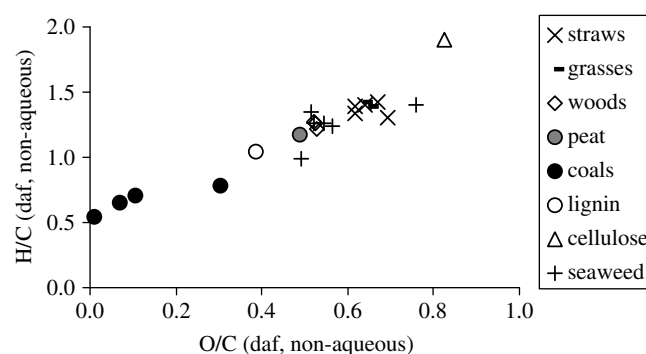
Fig. 1. Van Krevelen diagram for macroalgae compared to other solid fuels.

alginic acid, laminarin, mannitol, methylpentosans, and other sugars. The high protein content is associated with higher nitrogen content. There is no lignin and no cellulose, and the main component is the carbohydrate fraction.

The ash contents are given in Table 1 and the metal analysis given in Table 2. Ash content varies in different species and also varies with geographical location and season (Rupérez, 2002). For these samples the ash contents fall in the range (12–36 wt%). *C. filum* is lower in ash content than the other species and is comparible to *Miscanthus* in this respect; *M. Pyrifera* has the highest ash content. The compositions of the ash are different from terrestrial biomass. In fact, determination of the ash content can be problematic as the ash contains a significant amount of volatile inorganics. Different methods produce significant variation in ash values. For this paper two different methods are used and the British Standard measurements are utilised for further calculation of ash composition. Characterisation of the ash, and investigation of the reasons for the difficulty in reliable ash determination needs further study and is a planned future research activity.

For these samples, the seaweed ash contains larger amounts of macro-minerals (Na, K, Ca, P, Si, and Mg and trace elements (Fe, Zn, Mn, Al, and Cu) than terrestrial biomass. Seaweed ash is known to contain sodium carbonate, potassium carbonate, and calcium carbonate

Table 2
Macroalgae metals analysis (as received)

Material	Metal contents (ppm)																
	Al	Ca	Cu	Fe	K	Mg	Mn	Na	Cr	P	Pb	Si	Sr	Zn	As	Cd	Se
Fucus vesiculosus[a]	1275	10,650	13.7	2420	37,450	7710	66.2	29,350	7.2	24,970	6.0	3060	480	282	69.9	2.4	69.8
Chorda filum[a]	294	13,450	11.2	2095	6885	8185	7.6	20,850	2.7	9770	6.5	1275	1145	84	46.1	0.8	27.1
Laminaria digitata[a]	186	10,600	17.5	1980	36,600	9325	29.3	43,300	2.3	8750	7.0	1215	524	205	77.5	1.1	31.5
Fucus serratus[a]	1520	21,750	14.4	2860	24,900	8435	291	23,050	9.0	14,410	13.4	3705	1155	288	81.9	2.0	30.3
Laminaria hyperborean[a]	545	11,600	129.5	2095	68,450	7545	45.0	25,150	5.3	4870	3.6	1835	593	1225	126	1.6	26.6
Macrocyctis pyrifera[a]	1830	31,950	15.2	3500	26,250	10,600	24.9	54,300	17.2	12,650	1.8	5875	1320	70	57.4	6.5	31.7
Oat straw	51	1088	–	24	20,353	332	–	2710	–	354	–	213	–	12	–	0.02	–
Miscanthus	120	1340	–	100	3150	340	–	130	–	300	–	690	–	24	–	–	–
Willow coppice	50.0	11,020	38	137	3770	1350	181	246	–	471	63.1	6.2	–	196	–	2.46	–

[a] Water washed prior to air drying.

(Rupérez, 2002), and, in general, the brown seaweeds have a higher ash content than other types. The metals species in biomass are important in conversion processes because of their impact on slagging, fouling and other ash related problems. Some of the important inorganics in combustion applications include Si, K, Ca, Mg, Na, Al, P, S, and Cl because these species dictate the ash behaviour. From the data presented in Tables 1 and 2 the ash composition can be calculated and this data is given in Table 3. The potassium and sodium content dominate the ash components and as such would present severe problems for the potential use of this fuel in combustion or gasification. The alkali index is given in Table 3 to provide an estimation of the fouling potential of the ash, and expresses the amount of alkali oxide in the fuel per unit of energy (kg alkali/GJ). As a guide, Jenkins et al. (1998) suggests that a value of 0.17 kg alkali/GJ is the threshold for probable fouling, and a value of 0.34 kg alkali/GJ leads to virtually certain fouling. The macroalgea studied have alkali index in the range 16–82. Thus it is clear, even from this simple analysis, that unless further washing were utilised to reduce the alkali levels, these macroalgae could not be used in dedicated systems without encountering problems in component failure. Hence these fuels should only be considered for combustion (and gasification) processes as a component of a carefully monitored fuel blend, so that ash chemistry is controlled favorably. More work is required to assess the effects of seasonal variation of fuel properties, since it is expected that the samples analysed were at there point of highest ash content and protein content. Sampling in the autumn month may improve the properties significantly and is the subject of on-going research. Furthermore, the ash components may be favourable for other conversion processes such as liquefaction or digestion and the former process is also currently under study.

Previous potash production has been implicated with a number of environmental pollution issues. Given the concentrations of arsenic in seaweeds can be as high as 100 mg/kg, the kelp industry may have contributed to arsenic contamination, particularly in areas where seaweed was burnt for the production of potash. Some of the trace heavy metals are lost as volatiles during combustion (Riekie et al., 2006). This leads to a transformation of organic arsenic (as arsenosugars) in the original seaweeds to inorganic forms which are considerably more toxic. The analysis shown in Table 2 indicates that some of the studied seaweeds have high arsenic levels (as high as 100 ppm). Selenium has similar chemistry to arsenic and its concentration is also high. Of significance also is the high strontium content.

3.2. Combustion behaviour

Thermogravimetric analysis (TGA) methods in nitrogen and air have been developed previously (Jones, 2004) to study combustion behaviour of biomass. Combustion can be described as an initial devolatilisation and volatile combustion followed by slower burning of the char. TGA analyses in nitrogen represents the initial pyrolysis step (Fig. 2) and indicates significant differences in pyrolysis behaviour. The onset of pyrolytic decomposition occurs at a lower temperature for kelp compared to terrestrial biomass with high cellulosic content (straws and grasses) or high lignin content (woody biomass). The main weight loss is in the region of 250 °C consistent with higher carbohydrate content, although the catalytic influence of the inherent metals cannot be overlooked either. Pyrolysis undergoes a stepwise process corresponding to the biochemical composition. The first step of thermal degradation of lignocellulosic material is attributed to the decomposition of hemicellulose and the initial stage of degradation of cellulose (occurring between 200 °C and 270 °C), while the second step is attributed to the degradation of lignin and the final degradation of cellulose (occurring between 270 °C and 370 °C). The stepwise mass loss for macroalgea represents the decomposition of carbohydrate (180–270 °C) and the protein content (320–450 °C). TGA-pyrolysis shows a gradual loss in mass above 500 °C which can be attributed to volatile metal loss and carbonate decomposition. A significant proportion of inorganic material in kelps decompose at 750–800 °C, probably a consequence of metal carbonates.

Table 3
Calculated ash analysis of macroalgae

		Fucus vesiculosus	*Chorda filum*	*Laminaria digitata*	*Fucus serratus*	*Laminaria hyperborea*	*Macrocyctis pyrifera*
SiO_2	%	1.26	1.02	0.44	1.50	0.50	1.51
Al_2O_3	%	0.93	0.42	0.12	1.09	1.46	0.83
Fe_2O_3	%	1.33	2.24	0.95	1.55	7.91	1.20
CaO	%	5.73	14.09	4.97	11.54	16.53	10.72
Na_2O	%	15.20	21.04	19.56	11.78	6.10	17.56
MgO	%	4.91	10.16	5.18	5.30	40.22	4.22
K_2O	%	17.34	6.21	14.78	11.38	0.50	7.59
Mn_3O_4	%	0.04	0.01	0.01	0.15	0.03	0.01
P_2O_5	%	21.99	16.76	6.72	12.52	5.44	6.95
	Total	68.73	71.94	52.73	56.83	79.12	50.59
Alkali index		4.951	2.034	5.024	3.248	6.163	6.027
kg alkali/GJ		20.30	37.25	82.09	16.02	49.46	17.67
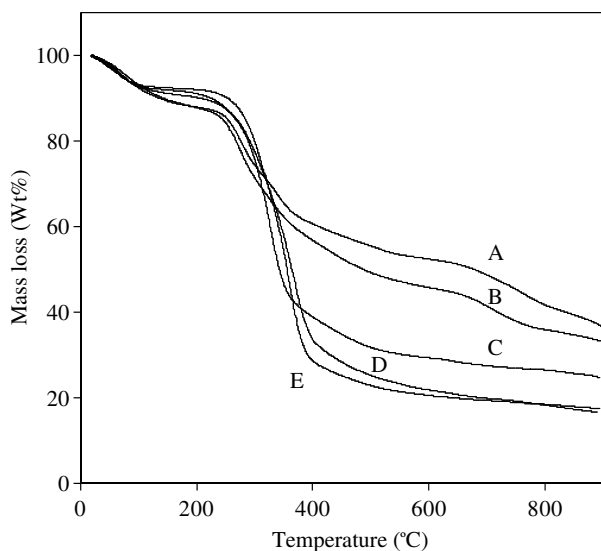
Fig. 2. Thermal gravimetric analysis of fuels in nitrogen showing mass loss at 25 °C min^{-1} for A. *Macrocystis pyrifera*, B. *Fucas Vesticulosus*, C. Oat straw, D. Willow, and E. *Miscanthus*.

Thermogravimetric analysis in air represents the burning profiles (Fig. 3) and indicates a more complex degradation route for macroalgae. Only three macroalgae are shown, but similar features were present in the burning profiles of all the seaweeds. Initial onset of burning is similar to oat straw, slightly lower than the higher lignin biomass, however char formation appears to be significantly higher. A stepwise profile is observed attributed to carbohydrate, fibre, lipids and protein. There again appears to be significant weight loss at higher temperatures which is attributed to inorganic decomposition. There is more fixed carbon in the macroalgae which forms a more stable char
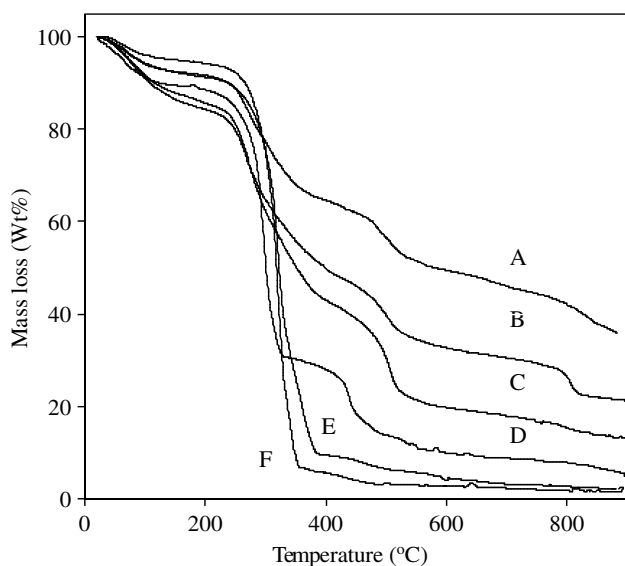
perhaps because of high K levels which is known to increase char yield (Antal and Grønli, 2003). There is no doubt that alkali metals influence pyrolysis and combustion behaviour although the ash chemistry appears to be more complex than for terrestrial biomass. A catalytic effect due to presence of potassium in the biomass samples (willow SRC, wheat straw) was observed during combustion experiments in a DTA (Nowakowski and Jones, 2006) and methane–air flame (Darvell et al., 2005). Potassium catalyses both volatile combustion and char burn-out reactions (Jones et al., 2007).

3.3. Flash pyrolysis behaviour
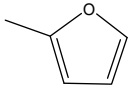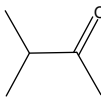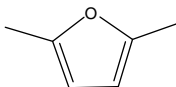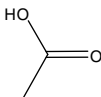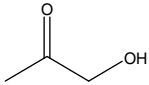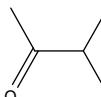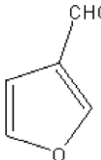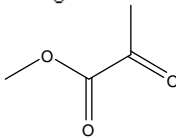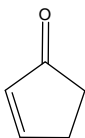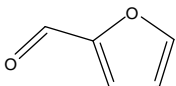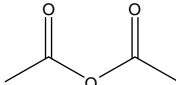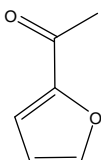
The pyrolysis process of biomass is highly complex and depends on several factors such as composition, heating rate, and content of inorganic material (Nowakowski and Jones, 2006). At low heating rates (<100 °C/min) many biomass materials decompose in well discernible stages of: (i) moisture evaluation, (ii) hemicellulose decomposition, (iii) lignin and cellulose decomposition. Under flash pyrolysis conditions (>100 °C/s) the decomposition of the individual components overlap, however it is still possible to assimilate the origin of different products to the different biomolecules.

Pyrolysis-gc-ms is a well documented technique for studying the decomposition of lignocellulose type materials. Pyrolysis-gc-ms of *M. pyrifera* has been performed at 500 °C. The degradation products can be classified as being either carbohydrate, protein or polyphenolic in origin and are listed in Table 4 (carbohydrate) and Table 5 (protein, lipid, and polyphenolic) together with their structures. A similar pattern is seen for all samples although the distribution of certain peaks can vary significantly. In particular it was noted that the lipid content can vary from species to species. A wide range of furan derivatives is observed, which are more numerous than those from terrestrial biomass although some similar bio-markers such as furfural and furaldehyde are present in both.

The main differences between the two types of biomass are that the macroalgae produce (a) a significant increase in nitrogen containing compounds, (b) linear chain alcohols and (c) an absence of methoxyphenols. In addition, the main sugar structural unit for macroalgae appears to be di-anhydro mannitol and there are a number of interesting sterol type structures present such as iso-sorbide. The nitrogen compounds are mainly analogues of pyrrole and indole.
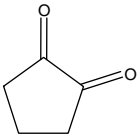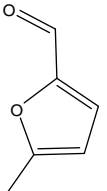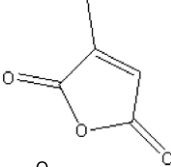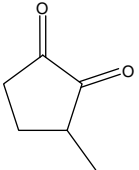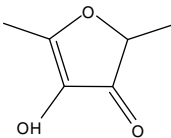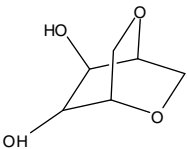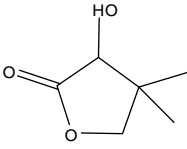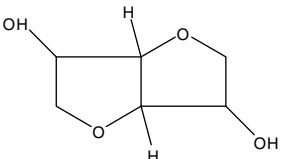
In contrast, the py-gc-ms of terrestrial biomass show the presence of phenolic fragments such as methoxyphenols attributed to lignin pyrolysis. It is clear that the alkyl substituted methoxyphenols from lignin pyrolysis are dominant in the pyrolysis profiles of the terrestrial biomass and almost absent in those of macroalgae. There are however small amount of alkyl phenols present which are thought to derive from polyphenolic molecules such as phlorotannins (Van Heemst et al., 1996) as macroalgae does not

Fig. 3. Thermal gravimetric analysis (TGA) of fuels in air showing mass loss at 25 °C min^{-1} for A. *Macrocystis pyrifera*, B. *Laminaria digitata*, C. *Fucas Vesticulosus*, D. Oat straw, E. Willow, and F. *Miscanthus*.

Table 4
Main products of polysaccharide origin identified from pyrolysis of *M. pyrifera* at 500 °C using pyrolysis-gc-ms

Peak number	Compound	Structure	Formula	Molecular weight
1	Acetone		C_3H_6O	58
2	2-Methylfuran		C_5H_6O	82
3	3-Methyl-2-butanone		$C_5H_{10}O$	86
4	2,5-Dimethylfuran		C_6H_8O	96
5	Acetic acid		$C_2H_4O_2$	60
8	1-Hydroxy 2-propanone		$C_3H_6O_2$	74
10	3-Hydroxy-2-butanone		$C_4H_8O_2$	88
13	3-Furaldehyde		$C_5H_4O_2$	96
15	Propanoic acid 2-oxo, methyl ester		$C_4H_6O_3$	102
16	Cyclopenten-1-one		C_5H_6O	82
17	Furfural		$C_5H_4O_2$	96
19	2-Propanone, 1-(acetyloxy)		$C_5H_8O_3$	116
21	Ethanone 1-(2-furanyl)		$C_6H_6O_2$	110

(*continued on next page*)

Table 4 (*continued*)
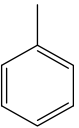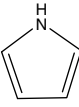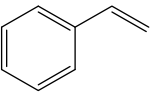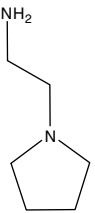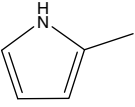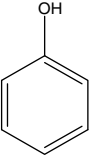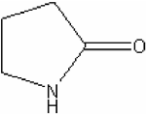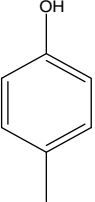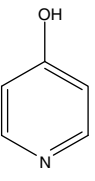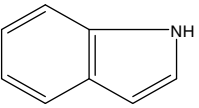
Peak number	Compound	Structure	Formula	Molecular weight
23	1,2-Cyclopentanedione		$C_5H_6O_2$	98
22 or 24	5 Methyl -2-furaldehyde		$C_6H_6O_2$	110
26	Furandione, 3-methyl		$C_5H_4O_3$	112
27	1,2-Cyclopentanedione, 3-methyl		$C_6H_8O_2$	112
30	2,5-Dimethyl-4-hydroxy-3(2H)-furanone		$C_6H_8O_3$	128
35	Dianhydro mannitol		$C_6H_{10}O_4$	146
38	Pantolactone		$C_6H_{10}O_3$	130
42	Isosorbide		$C_6H_{10}O_4$	146

contain lignin. Lignin pyrolysis is known to produce compounds such as phenol, 2-methoxyphenol, 2-methoxy-4-vinylphenol, vanillin, 2,6-dimethoxyphenol, 2-methoxy-4-(1-propenyl)-phenol, 4-methoxy-3-(methoxymethyl)-phenol, 4-hydroxy-3-methoxy benzoacetic acid, 4-hydroxy-3,5-dimethoxybenzaldehyde, 2,6-dimethoxy-4-(2-propenyl)-phenol. The remaining material is consistent with a carbohydrate degradation route although there is still significant differences to cellulose.

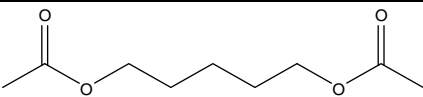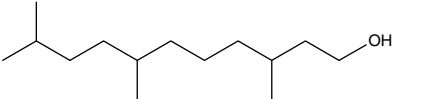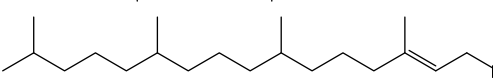Alginates are linear unbranched polymers containing (1,4)-linked D-mannuronic acid (M) and (1,4)-linked L-guluronic acid (G) residues. This bio-polymer breaks down in a different way to cellulose which consists of D-glucose molecules joined by β-glycosidic linkages. There are two main types of carbohydrates in brown seaweed, those with beta-1,3 linkages (e.g. laminarin and mannitol) defined as sugars and those with beta-1,4 linkages (e.g. amylopectin, amylose) roughly equivalent to starch in land plants. These structural differences explain the formation of anhydro mannitol rather than levoglucosan. Pyrolysis of kelp therefore represents a potential source of chemicals or could be used for the production of transport fuels. The high pro-

Table 5
Main products of protein, lipid and polyphenolic origin identified from pyrolysis of *M. pyrifera* at 500 °C using pyrolysis-gc-ms

Peak number	Compound	Structure	Formula	Molecular weight
9	Toluene		C_7H_8	92
11	Pyrrole		C_4H_5N	67
14	Styrene		C_7H_8	104
12	1-Pyrrolidine ethanamine		$C_6H_{14}N_2$	114
18	2-Methyl-1H-pyrrole		C_5H_7N	81
29	Phenol		C_6H_6O	94
33	2-Pyrrolidinone		C_4H_7NO	85
32	4, Methyl phenol		C_7H_8O	108
36	4-Pyridinol		C_5H_5NO	95
41	Indole		C_8H_7N	117

Table 5 (continued)

Peak number	Compound	Structure	Formula	Molecular weight
44	1,5-Diacetoxypentane		$C_9H_{16}O_4$	188
45	1-Dodecanol, 3,7,11-trimethyl		$C_{15}H_{32}O$	228
46	3,7,11,15-Tetramethyl-2-hexadecen-1-ol		$C_{20}H_{40}O$	296

portion of furans and a lower proportion of phenolic compounds could be a major advantage, as the phenolic material is much more resistant to hydrodeoxygenation.

The yields of char during pyrolysis are high and there maybe applications for activated carbons or sorbents which maybe activated naturally relative to low K biomass. Char yields during flash pyrolysis are significant and follow the order Kelp > Willow > Oat straw. Char yields are lower for flash pyrolysis than for slow ramp rate pyrolysis.

3.4. General discussion and recommendations

Direct combustion of a relatively high chlorine, high ash, low CV and high moisture content biomass does not appear an attractive option. For Gasification, mineral matter may play a catalytic role in tar cracking although an increase in alkali salts containing Na would lower the flow temperature of the slag, and the chlorides have an increased tendency to vaporise. This technology is currently being investigated in Japan but macroalgae may require pretreatment prior to utilisation. Pyrolysis is normally associated with dry fuels, although interesting pyrolysis products are formed and the production of chemicals maybe a more viable option for macroalgae using this route. Char formation is high, and the properties of this char require further investigation. The inherent metals in the kelp clearly catalyse the pyrolysis process. However, the fate of heavy metals during pyrolysis maybe a restricting issue and this too requires further investigation. The fate of nitrogen and chlorine are important, although scope exists for a range of useful compounds which may perhaps exhibit medicinal importance.

Utilisation of kelp for energy rests on obtaining a sufficient supply of biomass. Kelp can either be harvested from naturally occurring beds of seaweed (wild) or cultured (or farmed) seaweeds. In both cases, utilisation for energy would compete for usage in the food and colloid industry. There are fears that over harvesting of kelp beds may lead to the damaging of ecosystems which many other species rely on. It has even been suggested that current extraction is reducing population irreversibly. As a consequence of such concerns, whether justified or not, many countries operate a strict licensing system to control the over harvesting of kelp beds. Britain and Ireland have significant stands of wild kelps, although there is little culture of seaweeds. Environmental impact and economic assessments are required to ascertain the relative merits of farming versus wild harvest and the relative amounts that might be supplied by each route.

4. Conclusions

Significant differences in fuel properties exist between kelps and terrestrial biomass. The heating value is lower than that of the terrestrial energy crops (cf. 14–16 MJ kg^{-1} to 17–20 MJ kg^{-1}), since, in general, the ash content is higher. Consequently, the metal contents (especially alkali metals) are, for the most part, higher in the seaweeds studied here compared to the terrestrial biomass. Total halogen content is in the range 0.5–11% in kelps which is also significantly higher than terrestrial biomass (1–1.5%). Thus it is clear that unless washing were utilised to reduce the alkali levels, these macroalgae could not be used in dedicated systems without encountering problems in component failure. However, mineral matter is known to vary during the growth cycle of seaweeds and further investigation of this is warranted to assess the potential farming strategies to control this.

Flash pyrolysis of macroalgae produces interesting compound fingerprints and a range of low molecular weight oxygenated and nitrogen containing compounds. The fate of nitrogen is potentially problematic in using these as fuels and some further de-nitrogenation maybe necessary. There is scope however for the production of useful chemical commodities, perhaps with high value. Unlike terrestrial biomass, macroalgae does not contain as much phenolic material owing to the absence of lignin type materials. The carbohydrate content produces similar but different compounds to those from cellulose.

The most suitable conversion technologies for macroalgae will most likely be those which are most tolerant to the ash components in the fuel. As a consequence, hydrous pyrolysis or digestion methods may be more for exploitation of these resources for fuels and chemicals than anhydrous pyrolysis or combustion/gasification. The metals

present produce a significant catalytic effect on pyrolysis and this requires further investigation.

Acknowledgements

References

Abbott, I.A., 1982. Seaweeds and their uses. Aquatic Botany 12, 389–390.

Antal, M.J., Grønli, M., 2003. The art, science, and technology of charcoal production. Industrial and Engineering Chemistry Research 42, 1619–1640.

Aresta, M., Dibenedetto, A., Barberio, G., 2005. Utilisation of macro-algae for enhanced CO_2 fixation and biofuels production: development of a computing software for an LCA study. Fuel Processing Technology 86, 1679–1693.

Brown, L.M., Zeiler, K.G., 1993. Aquatic biomass and carbon dioxide trapping. Energy Conversion and Management 34, 1005–1013.

Cadée, G.C., 1992. Seaweed resources in Europe: uses and potential. Aquaculture 107 (4), 395–396.

Chynoweth, D.P., Turick, C.E., Owens, J.M., Jerger, D.E., Peck, M.W., 1993. Biochemical methane potential of biomass and waste feedstocks. Biomass and Bioenergy 5 (1), 95–111.

Chynoweth, D.P., Owens, J.M., Legrand, R., 2001. Renewable methane from anaerobic digestion of biomass. Renewable Energy 22, 1–8.

Darvell, L.I., Hrycko, P., Jones, J.M., Nowakowski, D.J., Pourkashanian M., Williams, A., 2005. Impact of minerals and alkali metals on willow combustion properties. In: Proceedings of the World Renewable Energy Congress, Aberdeen, pp. 584–589.

Gellenbeck, K.W., Chapman, D.J., 1983. Seaweed uses: the outlook for mariculture. Endeavour 7 (1), 31–37.

Jenkins, B.M., Baxter, L.L., Miles, T.R., Miles, T.R., 1998. Combustion properties of biomass. Fuel Processing Technology 54 (1–3), 17–46.

Jones, J.M. et al., 2004. Towards biomass classification for energy applications. In: Proceedings of the International Conference on Science and Thermal and Chemical Biomass Conversion, Victoria, Canada.

Jones, J.M., Darvell, L.I., Bridgeman, T.G., Pourkashanian, M., Williams, A., 2007. An investigation of the thermal and catalytic behaviour of potassium in biomass combustion. In: Proceedings of the Combustion Institute, vol. 31, pp. 1955–1963.

Maeda, K., Owada, M., Kimura, N., Omata, K., Karube, J., 1995. CO_2 fixation from the flue gas on coal-fired thermal power plant by microalgae. Energy Conversion and Management 36, 717–720.

Marinho-Soriano, E., Fonseca, P.C., Carneiro, M.A.A., Moreira, W.S.C., 2006. Seasonal variation in the chemical composition of two tropical seaweeds. Bioresource Technology (18), 2402–2406.

McHugh, D.J., 2003. A guide to the seaweed industry. FAO Fisheries Technical Paper 441. Food and Agriculture Organisation of the United Nations, Rome.

Miao, X., Wu, Q., Yang, I.C., 2004. Fast pyrolysis of microalgae to produce renewable fuels. Journal of Analytical and Applied Pyrolysis 71, 855–863.

Minowa, T., Dote, Y., Sawayama, S., Inoue, S., Yokoyama, S., 1994. Recovery of liquid fuel from hydrocarbon-rich microalgae by thermochemical liquefaction. Fuel 73, 1855–1857.

Nowakowski, D.J., Jones, J.M., 2006. Influence of potassium catalysis on pyrolysis and combustion behaviours of wheat straw. In: Proceedings of the 19th International Symposium on Combustion Processes, Wisla, Poland.

Raiko, M.O., Gronfors, T.H.A., Haukka, P., 2003. Development and optimization of power plant concepts for local wet fuels. Biomass and Bioenergy 24 (1), 27–37.

Riekie, G.J., Williams, P.N., Raab, A., Meharg, A.A., 2006. The potential for kelp manufacture to lead to arsenic pollution of remote Scottish Islands. Chemosphere 65 (2), 332–342.

Renewable biological systems for alternative sustainable energy production, 1997. Food and Agriculture Organization of the United Nations (FAO), Agricultural Services Bulletin – 128 ISBN 92-5-104059-1.

Ross, A.B., Jones, J.M., 2005. Comparison of fuel properties of terrestrial and marine biomass. In: Proceedings of the XIX International Symposium on Combustion Processes, 30 August – 2 September, Beskidy, Poland.

Rupérez, P., 2002. Mineral content of edible marine seaweeds. Food Chemistry 79 (1), 23–26.

Sánchez-Machado, D.I., López-Cervantes, J., López-Hernández, J., Paseiro-Losada, P., 2004. Fatty acids, total lipid, protein and ash contents of processed edible seaweeds. Food Chemistry 85 (3), 439–444.

Sawayama, S., 1999. Possibility of renewable energy production and CO_2 mitigation by thermochemical liquefaction of microalgae. Biomass Bioenergy 17 (1), 33–39.

Scragg, A.H., Illman, A.M., Carden, A., Shales, S.W., 2002. Growth of microalgae with increased calorific values in a tubular bioreactor. Biomass and Bioenergy 23 (1), 67–73.

Song, Q., Peng, J., Chengkui, T., 2006. Transforming Kelp into a marine bioreactor. Review, Trends in Biotechnology 23 (5), 264–268.

Tarwadi, S.J., Chauhan, V.D., 1987. Seaweed biomass as a source of energy. Energy 12 (5), 375–378.

Van Heemst, J.D.H., Peulve, S., De Leeuw, J.W., 1996. Novel algal polyphenolic biomacromolecules as significant contributers to resistant fractions of marine dissolved and particulate organic matter. Organic Geochemistry 24 (6/7), 629–640.

Wang, J., Wang, G., Zhang, M., Chen, M., Li, D., Min, F., Chen, M., Zhang, S., Ren, Z., Yan, Y., 2006. A comparative study of thermolysis characteristics and kinetics of seaweeds and fir wood. Process Biochemistry 41 (8), 1883–1886.

Wise, D.L., 1981. Probing the feasibility of large scale aquatic biomass energy farms. Solar Energy 26 (5), 455–457.