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Thermochemical characterization of brown seaweed, *Laminaria digitata* from UK shores

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ABSTRACT

Brown algae, *Laminaria digitata* samples were collected over six-month intervals within a year (January, July and December 2015) and assessed for a range of thermochemical properties. Initial pyrolysis rates using thermogravimetric analysis (TGA) were carried out to assess their proximate characteristics, ranging from moisture content (MC) (3.48%–4.10%), volatile content (VC) (56.64–56.23%), char (11.80–12.76%) and fixed carbon (27.87–29.95%). Analysis by pyrolysis gas chromatography–mass spectrometry (Py–GC/MS) identified sixty four compounds present in all samples, twenty which have been previously reported as major pyrolysis products of *Laminaria digitata.* ^{1}H NMR analysis of sodium alginate fractions extracted from the samples was used to characterise the monad, diad, triad frequencies and average block length of the alginate. Results of the monad frequencies F_M (0.36–0.46) and F_G (0.54–0.64) are consistent with reported values in literature. The *Laminaria digitata* alginate also showed values that are in agreement with most reported literature for both diad frequencies, homopolymeric mannuronic (F_{GG} = 0.19–0.25) and guluronic (F_{MM} = 0.33–0.47) blocks with alternating block fractions of (F_{GM} = 0.17–0.21) and (F_{MG} = 0.17–0.21), respectively. The M/G ratio value of 1.17–1.80 has been stated for alginates that can be used to produce soft and elastic gels rather than brittle ones. Furthermore, the computed triad frequencies results are (F_{GGG} = 0.14–0.17, F_{MGM} = 0.11–0.13, F_{GGM} = F_{MGG} = 0.05–0.09) and the average block lengths are (N_G = 2.15–2.22 and N_M = 2.61–3.85).

1. Introduction

There has been a significant increase in the utilization of biomass fuels as a result of the problems associated with the use of fossil fuels and societal interest in climate change. Biomass are carbon neutral materials regarded as "green" alternative to fossil fuels [1], and can be used to produce liquid transport fuels, renewable electrical or heat energy and chemicals [2,3]. They are biological in nature comprising all living matter [4], and are derived from marine algae, terrestrial plants or animal manure [3]. Various conversion routes are used to extract the chemical carbon energy trapped in these biomass into useful energy products mainly biofuels (bioalcohols, biodiesel, bio-oils and biogas) [5]. Energy extraction methods include direct combustion, pyrolysis, and gasification, hydrothermal treatments, fermentation to bioethanol or biobutanol and anaerobic digestion (AD) [6]. However, there are significant short comings associated with the different biomass categories in their use for energy conversion purposes.

The life cycle assessment of terrestrial based biomass final products shows that it rather exacerbates climate change [7], with direct and indirect land use for energy crop cultivation inducing both high carbon debt and water consumption [8,9]. Biomass from *energy crops* such as corn, sugarcane and soybeans are widely used for large-scale biofuels production because of well-established farming practices which are simple and cheap for starch, oil and sugar release [10], but there are concerns with respect to food scarcity, high prices for food commodities and land pollution [11]. These concerns led to research and renewed interest in marine based biomass mostly macroalgae regarded as "silver bullet" with potential as an alternative to fossil fuels. Marine biomass makes more than 50% of global primary biomass production [2]. The macroalgae of particular interest are the brown algae (*Phaeophyta*), principally the kelps [12]. Macroalgae have many advantages over other biomass types in their utilization for energy conversion: they do not need land or fresh water for cultivation [13], and have higher productivity rates than most terrestrial biomass such as corn and switch grass [14]. They are characterized as having no lignin, low cellulose and lipid content [7], although the presence of secondary walls and lignin within the cells of red algae have been reported [15]. Macroalgae can convert solar energy into chemical energy with photosynthetic efficiency up to 6–8% compared to 1.8–2.2% terrestrial biomass [16]. As photoautotrophic plants they produce and store organic carbon utilising

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CO_2 and HCO_3^-, that can be used as resources needed for biorefinery [17]. Because seaweeds lack many of the distinct organs found in terrestrial plants, whole parts are available as a biomass source [18]. They have a lower risk for competition for food and energy than other land-based crops [19,20]. Growing and harvesting of macroalgae remove nutrients from water and hence reduces eutrophication [21]. In assessing the carbon balance of macroalgae biofuel from aquaculture, there is potential to include carbon sequestration associated with the growth of seaweed [19]. It has been estimated that their cultivation along coastlines (China and USA) can sequester about 1 billion tonnes of carbon annually [14]. Also, advances in macroalgae cultivation technologies could potentially increase production from three to 10-fold, with a corresponding decrease in the area needed for cultivation to meet specified production goals [22]. These advantages have led to a number of studies being carried out on macroalgae to access its bioenergy potential [23]. Macroalgae based biomass from marine resources has the potential to partially and fully displace terrestrial based biomass for sustainable biorefinery via bioenergy and biomaterials production [7]. Biomaterials that can be produced from macroalgae include alginates, carrageenans, agars and phycocolloids, also they are used as food, fertilisers and cosmetics ingredients [6]. Macroalgae contains major structural polysaccharides (biopolymer) such as cellulose, agar, carrageenan, starch, laminaran, mannitol, alginate and fucoidan that are potentially biochemical feedstocks for production of liquid biofuels [10,22,24,25]. Some of these compounds are unique, and their distribution differs across the major macroalgal taxonomic groups of brown, green, and red seaweeds [10,22].

Brown algae are the largest of all seaweed, found in shores and shallow seas in temperate regions all around the world, having their brown or olive- green colour due to pigments of chlorophyll "a" and 'c', β-carotene and xanthophyll, fucoxanthin [26–28]. Typically, they are made of hold fast, which clings to rocks as roots, a more or less elongated stalk known as stipe, as stem, and an entire/lobed blade, the fronds, as leaves [29–31]. Brown seaweeds are used as food and serve to provide a habitat for other organisms in the marine environment. There are about 1500 − 2000 known species [28,32]. The intertidal and shallow subtidal seas around Britain contain about 7% of the world's red, green and brown seaweed species [33]. Since, the UK has a coastline of about 31,400 km surrounding it and its main outlying islands [2], this makes this resource an attractive renewable energy source. *Laminaria digitata* utilised in this work has been described as a highly prevalent kelp growing off the coast of the UK, but has rarely been considered as a source of biomass to date [2]. The distribution of *Laminariales* in Britain, are found in dominating rocky shores at, or just below low water mark. Kelp is the common name for *Laminaria*, found typically at depths of 8–30 m in the north Atlantic and are considered optimal for bioconversion to energy [19]. The kelps are the largest growing macroalgal species within the Phaeophyceae and in the Atlantic waters surrounding the UK, the kelps are primarily members of the *Laminariales* order, growing up to 4 m in length [34]. Brown seaweed species generally dominate the flora in temperate seas and their relative abundance on the sublittoral zone of the British coastline make them a substrate of choice for anaerobic digestion [35]. It has been suggested there are approximately 100,000 ha of kelp forests in UK waters which could be commercially harvested [19]. The brown seaweed kelps are most affected by rising water temperature because sexual reproduction (gamete formation) in most kelps will not occur above 20 °C [36]. Within three European species of Laminaria, 15 °C has been reported as optimal growth temperature [37]. Among the seaweed species, brown seaweeds are considered the single largest macroalgae resource and are a likely candidate for energy processing [38]. The primary carbohydrates in brown seaweeds are Alginate, Laminarin, Mannitol, Fucoidans and cellulose [10,22,39]. A semi-speculative or hypothetical model of the structure of cell wall of brown algae is presented in Fig. 1 [39,40].

In the use of macroalgae as a promising feedstock, convenient for biofuels production [4], biogas production through AD is one of the most direct routes [41] with brown macroalgae being the most favourable for large scale production to meet biofuels goals of the future [42]. AD of macroalgae has shown high yields and conversion rates [43] but has weighty short comings of remarkably slower rates and incomplete process digestion compared to other thermal processes [23].

Various technologies are continuously been investigated for conversion of biomass into energy products (biofuels, power and chemical commodities). In the UK for instance as reported by Ross et al. [23] legislation supporting renewable obligatory credit has been a vehicle for increased utilization of biomass in the energy sector. Thermal decomposition reactions play an increasingly vital role during several of the biomass utilization processes [44]. The two main thermochemical processes for converting biomass into energy and chemical products are gasification and pyrolysis [45]. Biomass fuels contain a wide range of pyrolyzing species [44] and thermochemical conversion methods such as pyrolysis has been used to produce bio-oil as replacement for fossil fuel based diesel [34]. Other studies on thermal behaviour of marine macroalgae have also been carried out [23,46]. Until recently, attention has rarely been paid to thermochemical conversion of kelp [23]. Recently, a sizeable number of studies has demonstrated the potential of algae as a renewable energy resource using pyrolysis [47]. The thermochemical conversion of biomass into fuels; charcoal, bio-oil and gaseous products by heat under anaerobic conditions is known as pyrolysis [48,49]. Pyrolysis is regarded as an effective method to produce fuel from biomass [49]. TGA is often employed in pyrolysis studies to examine biomass thermal characteristics by measuring changes in mass as a function of temperature and time when biomass volatilizes under a controlled atmosphere [47]. The thermal conversion of brown algae using pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) and thermogravimetry (TGA) has been studied and their reactions products identified [50]. Their identification is through the detection of 'fingerprint' compounds by Py-GC/MS which has been used to determine the presence of certain carbohydrates in seaweeds [51]. During the pyrolysis characterization of carbohydrates components (alginic acid, mannitol, laminarin and fucoidan) of brown macroalgae using Py-GC/MS predominantly furfural, 5-methyl 2-furancarbox-aldehyde and 2-methoxy-5-methyl thiophene, 1-(2-furanyl) ethanone and dianhydromannitol and 1,2-cyclopentanedione, 2-hydroxy-3-methyl 2-cyclopenten-1-one and acetic acid were identified [51]. In other studies ten consistent compounds; ethanone, pyrrole toluene; furfural; 1-(2-furanyl); dianhydromannitol; 5-methyl; 3-methyl; phenol; indole; 3, 7, 11, 15-tetramethyl-2-hexadecen-1-ol, 1, 2-cyclopentanedi-one were previously identified from pyrolysis of *Laminaria digitata* [23,34]. In brown algae, the kelps, alginate is the largest organic fraction and extracted for the production of alginate on an industrial scale [52]. They contain natural occurring biopolymers [53]. Alginate is a term used to describe the salts of alginic acid [54], and has been extracted from wracks such as *Laminaria digitata and hyperborea, Macrocystis pyrifera, Ascophylum nodosum and Saccharina latissima* [19,55]. The residues from such extraction processes also represent a raw material for renewable energy [6]. The majority of the polysaccharide in brown algae is alginic acid which is a polymer of 5-carbon acids, D-mannuronic (M-block) and L-guluronic acid (G-block) with the formula $(C_6H_8O_6)_n$ [51]. The M and G monomers constitute M-, G-, and MG- sequential block structures [55], with a $^4C_1$ and $^1C_4$ conformation giving generally three types of glyosidic linkages (diequatorial (MM), diaxial (GG), and equatorial-axial (MG) in the block structure [56]. The alginate is present as a salt form of the alginic acid (sodium, calcium and magnesium salts) and their extraction process is geared towards obtaining filtered and dried sodium alginate powder since both calcium and magnesium salts do not dissolve in water [54,57]. The pyrolytic behaviour of alginate acid and its salt (Na alginate) has been previously studied using TGA in an inert atmosphere [58]. From the result of their TGA curve both the alginic acid and its salt shows two decomposition steps which are attributed to loss of water (hydration) and polymer (decomposition), and for Na