Copper(II)-mediated thermolysis of alginates: a model kinetic study on the influence of metal ions in the thermochemical processing of macroalgae

J. S. Rowbotham¹, P. W. Dyer¹, H. C. Greenwell², D. Selby² and M. K. Theodorou³,⁴

¹Centre for Sustainable Process Chemistry, Department of Chemistry, ²Department of Earth Sciences, and ³School of Biological and Biomedical Sciences, Durham University, South Road, Durham DH1 3LE, UK
⁴Centre for Process Innovation, Wilton Centre, Wilton, Redcar TS10 4RF, UK

Thermochemical processing methods such as pyrolysis are of growing interest as a means of converting biomass into fuels and commodity chemicals in a sustainable manner. Macroalgae, or seaweed, represent a novel class of feedstock for pyrolysis that, owing to the nature of the environments in which they grow coupled with their biochemistry, naturally possess high metal contents. Although the impact of metals upon the pyrolysis of terrestrial biomass is well documented, their influence on the thermochemical conversion of marine-derived feeds is largely unknown. Furthermore, these effects are inherently difficult to study, owing to the heterogeneous character of natural seaweed samples. The work described in this paper uses copper(II) alginate, together with alginic acid and sodium alginate as model compounds for exploring the effects of metals upon macroalgae thermolysis. A thermogravimetric analysis–Fourier transform infrared spectroscopic study revealed that, unusually, Cu²⁺ ions promote the onset of pyrolysis in the alginate polymer, with copper(II) alginate initiating rapid devolatilization at 143°C, 14°C lower than alginic acid and 61°C below the equivalent point for sodium alginate. Moreover, this effect was mirrored in a sample of wild Laminaria digitata that had been doped with Cu²⁺ ions prior to pyrolysis, thus validating the use of alginates as model compounds with which to study the thermolysis of macroalgae. These observations indicate the varying impact of different metal species on thermochemical behaviour of seaweeds and offer an insight into the pyrolysis of brown macroalgae used in phytoremediation of metal-containing waste streams.

1. Introduction

Biofuels represent one of a number of renewable technologies that aim to alleviate an overdependence on fossil-derived hydrocarbons. However, in recent years, the social, financial, climatological, ecological and political impacts of certain biofuels, such as corn-derived ethanol and palm oil-based biodiesel, have been highly contested [1]. With this in mind, so-called ‘advanced’ biofuels, derived primarily from feedstocks such as waste and non-edible plant matter, have awakened interest from the scientific community and beyond [2].

Although advanced biofuels are naturally more sustainable than their earlier counterparts, there are inevitable technological difficulties associated with the requirement to treat complex, heterogeneous, multi-component feedstocks, which may be difficult to upgrade using conventional biomass processing techniques such as fermentation and anaerobic digestion [3]. Consequently, thermochemical processing methods such as pyrolysis, hydrothermal liquefaction and gasification (all of which use heat to convert the feed) have come to the fore as versatile treatment options [4]. In this context, a diverse range of raw materials have now been considered for the production of fuels and chemicals,
including woods [5], bagasse [6], rice husks [7], tyres [8], duck weed [9] and sewage sludge [10].

One type of feedstock that has demonstrated considerable potential in thermochemical processing are macroalgae [11–14]. Macroalgae, or seaweed, are a group of fast-growing aquatic organisms that include some 9000 species worldwide [15]. Owing to the need for structural flexibility in turbulent coastal environments, macroalgae consist predominantly of elastic polysaccharides such as laminarin, carrageenan, agarose and alginic acid [16,17]; a stark contrast to the rigid lignocellulosic support required by terrestrial flora. These differences in biochemical composition mean that macroalgae offer unique opportunities in terms of thermochemical processing and its resulting products compared with their land-based counterparts. Moreover, seaweeds have the added advantages of high photosynthetic efficiencies (up to four times greater than terrestrial plants) and not competing with forestry and agriculture for land and fresh water [18,19].

Phaeophyceae (brown macroalgae, of which the orders Laminariales and Fucales are colloquially known as kelp) are common around the coasts of northern Europe [16] with considerable interest in their utilization as a feedstock for manufacturing commodity chemicals, dating back to the early seventeenth century [20]. More recently, work has demonstrated that kelps (including Laminaria digitata) show promise in thermochemical processes such as pyrolysis, because of their abundance, the diverse range of products they can afford and their relatively low thermal decomposition temperatures [11,12]. However, comparative investigations of macroalgae in thermochemical applications are hampered by the inherent heterogeneous nature of the samples collected for study [11]. This is particularly problematic because both the carbohydrate and metal contents vary considerably as a function of season, geographical location, local environment, induced stress conditions and by species [21–23], meaning studies that examine only a single sample of seaweed can be severely restricted in the general applicability of their conclusions. Consequently, investigations that use appropriate model compounds rather than whole biomass are of interest. Such an approach circumvents the problems associated with natural variance in biochemical composition and reveals fundamental trends, including the origins of various products and the key decomposition temperatures of certain constituents, thereby allowing pyrolysis processes to be better understood and, ultimately, optimized [24].

A particular area where model compounds can assist is in the prediction of the thermochemical behaviour of a biomass feedstock as a function of metal content. This parameter is particularly important since the presence of naturally occurring metals has been found to influence greatly the pyrolysis behaviour of various biomass types [25,26]. For example, potassium ions have been demonstrated to alter the kinetics of thermolysis (lowering both the first-order activation energy and onset temperature of rapid pyrolysis) of short rotation willow coppice, as well as promoting the conversion of complex molecules such as levoglucosan to more simple compounds, including acetic and formic acid [26,27].

Despite the established impact of metal ions in biomass thermochemical processing, their role is generally not well understood and has only been investigated for a few types of feedstock. Developing such insights for macroalgae feedstocks where the metal concentrations can be remarkably high (of the order of 10–20% of the dry weight [12]) is imperative. Indeed, significantly, few of the investigations to date feature a full analysis of the metal profile in the feedstock [28–30]. However, it should be noted that these types of studies are complicated because samples of metal-free macroalgae are not readily accessible as metal ion extraction (by acid washing for example) typically results in significant alteration of the biomolecular matrix that is under investigation [31,32]. Furthermore, a number of recent studies have started to probe the effects of directly incorporating metal-based catalysts into various biomass pyrolysis processes (including macroagal studies [33]) with a view to influencing the resulting product distributions and selectivity [34,35]. Again, however, in order to optimize catalyst integration in an effective manner, a clear understanding of the nature and impact of naturally occurring metals is of great importance.

In order to circumvent the issues associated with macroalgal sample heterogeneity and metal ion removal for thermolysis studies, alginic acid (consisting of alternating blocks of unbranched binary copolymers of 1,4-linked α-α-mannuronic (M) and β-β-guluronic (G) acid residues) and the corresponding metal alginate salts constitute a promising set of compounds with which to model the effects of metals. Alginate materials not only constitute between 10 and 40 wt% of the dry weight of many common kelps [22], but they are also largely responsible for the metal sequestering properties of brown macroalgae (figure 1) [36]. Thus, studies of discrete metal alginate salts can be used to model macroalgal thermal degradation, exemplifying the effects of a particular metal ion on pyrolysis without the results being convoluted by processes related to the decomposition of other compounds in the rest of the biomass.

A number of studies have explored the effects of various metals on alginate thermal stability using thermogravimetric analysis (TGA), a technique that measures the volatilization of a sample by recording mass loss as a function of temperature [37–44]. However, many of these TGA-based investigations have been carried out under oxidative conditions, where combustion is the predominant reaction. Consequently, these studies are poor models for understanding pyrolysis behaviour, which requires an inert environment. However, one study by Ross and co-workers examined both pyrolysis (in a nitrogen atmosphere) and oxidation (in air) of alganic acid and the corresponding sodium and calcium salts [44]. This study showed that calcium alginate degrades at a higher temperature than the sodium counterpart, which decomposes at a temperature closer to that of the parent acid. Both salts generated pyrolysis products similar to those from alganic acid, although the sodium salt equivalent gives rise to a significantly higher proportion of cyclopentenene derivatives. These observations indicate the influence that other metal ions may have on pyrolysis kinetics (i.e. temperatures, rate of pyrolysis, Arrhenius parameters) and resultant products from alginites and, crucially, raise the question of the degree to which these effects are mirrored during the pyrolysis of whole macroalgal biomass.

The work presented here aims to further the understanding of the impact of metals, widening the present studies on alginate thermolysis with alkali and alkaline earth metals to include d-block elements, which are found in some seaweed samples at concentrations many thousands of times higher than the surrounding seawater [45]. Studies to probe such effects are complex because, despite the passive nature of the biosorption process, macroalgae show preferences for certain metals above others [28–30]. This is particularly important since the presence of naturally occurring metals in biomass feedstocks is known to influence greatly the pyrolysis behaviour of various biomass types [25,26]. For example, potassium ions have been demonstrated to alter the kinetics of thermolysis (lowering both the first-order activation energy and onset temperature of rapid pyrolysis) of short rotation willow coppice, as well as promoting the conversion of complex molecules such as levoglucosan to more simple compounds, including acetic and formic acid [26,27].

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others, with the relative affinities (shown in figure 2) having been determined for divalent metal species. The observed trend is not easily explained, but it is thought to originate from the so-called ‘egg box’ model of divalent cation binding to alginates [46], in which some M$^{2+}$ ions fit the anionic cavities provided by two parallel strands of β-D-mannuronic acid better than others (figure 3) [47]. Indeed, brown macroalgae harvested from copper-polluted water exhibit particularly high concentrations of Cu$^{2+}$ ions, which is a direct consequence of the high affinity of alginates for copper [48,49].

Accordingly, the following study will examine the effects of Cu$^{2+}$ ions on the slow pyrolysis (i.e. at a heating rate less than 50°C min$^{-1}$ [50]) of alginates via TGA. However, in addition to this, it is also desirable to analyse the degree to which these findings are applicable to the outcomes of the thermal treatment of samples of real seaweed biomass. In order to facilitate such a comparison, the metals inherently present in a sample of macroalgae can be almost completely ion exchanged with Cu$^{2+}$ ions by soaking the seaweed in a copper-containing solution and, subsequently, the resulting copper(II)-doped macroalgae can be subjected to the same TGA treatment as the model copper(II) alginate compound. This approach will allow for a wider discussion on the methodological validity of using model compounds for studying biomass pyrolysis and the importance of characterizing the full metal content of a feedstock prior to its thermal analysis, a practice that is not currently commonplace.

**Figure 1.** Schematic of the mode of uptake of various mono- and di-valent metallic ions found in seawater by α-L-guluronic acid and β-D-mannuronic acid, which polymerize to form alginic acid (and the corresponding alginate salts) in large quantities in brown macroalgae [36]. (Online version in colour.)

**Figure 2.** The affinity of alginic acid in *L. digitata* for various divalent cations [47].

$\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} > \text{Mn}^{2+} > \text{Mg}^{2+}$
Figure 3. The ‘egg box’ model of divalent cation bonding in alginic acid [46]. (Online version in colour.)

2. Materials and methods

Alginic acid (H-Alg) and sodium alginate (Na-Alg) were obtained in powdered form from Sigma Aldrich and used as received.

2.1. Preparation of copper(II) alginate (Cu-Alg)

Copper(II) alginate (Cu-Alg) was prepared via an ion exchange protocol by suspending sodium alginate (2.0 g) in a solution of Cu(NO₃)₂ (100 ml, 1.0 M) and stirring vigorously for 6 h at room temperature, according to the following reaction:

\[ 2\text{Na-Alg} + \text{Cu}^{2+} \rightarrow \text{Cu-Alg}_2 + 2\text{Na}^+ \] (2.1)

The resulting light blue gelatinous precipitate was subsequently isolated by filtration, washed thoroughly with deionized water and dried to a constant weight at 80°C, which led to the isolation of a dark green solid.

2.2. Thermal analysis of H-Alg, Na-Alg and Cu-Alg

The alginic acid and two metal alginate powders were ground and sieved to 250 μm. The three samples were then subsequently dried at 105°C overnight, immediately prior to the TGA experiments, in order to attain similar moisture contents since both the alginate materials and alginic acid are hygroscopic. TGA experiments were carried out on the dried, ground samples of the H-, Na- and Cu-Alg using a Perkin Elmer Pyris 1 analyser by loading 20.0 ± 0.5 mg of the sample evenly into a platinum pan and subsequently heating from 25 to 900°C at 5, 10, 20, 30 and 40°C min⁻¹ under a flow of dry N₂ at 50 ml min⁻¹. The first derivative of the TGA data yielded the differential thermogravimetric profile (DTG). Coupled thermogravimetric analysis–Fourier transform infrared spectroscopic (TGA-FTIR) analyses of the three alginate samples were also carried out by heating the powders to 1000°C at 10°C min⁻¹ on a TA Q500 V6.7 Build 203 coupled to a Nicolet IS 10 infrared spectrometer. Differential scanning calorimetry (DSC) analyses were conducted on a TA Instruments DSC analyser (Qi1000, v. 9.9, build 303) by placing 5.0 ± 0.5 mg of sample into an aluminium sample pan, crimping it shut and then heating from 30 to 500°C at 10°C min⁻¹ under a flow of dry N₂ at 50 ml min⁻¹. For comparison, TGA of powdered samples of Na₂CO₃, CaCO₃ and CuCO₃ (each obtained from Sigma Aldrich and used as received) was also undertaken.

2.3. Kinetic analysis

TGA of H-, Na- and Cu-Alg was carried out at five different heating rates (β), in order to determine the energy of activation (Eₐ) and pre-exponential factor (A) for the thermal degradation of the samples at certain points in the pyrolysis process. This was achieved by adopting a previously used method, based on the approach described below [51].

During thermolysis, a sample will lose mass through volatilization. Hence, a degree of conversion αₓ of the sample at a temperature Tₓ can be defined:

\[ \alpha_x = \frac{m_0 - m_x}{m_0 - m_m} \] (2.2)

where \( m_0 \) is the initial mass of the sample, \( m_x \) is the mass at temperature \( T_x \), and \( m_m \) is the final mass. Thus, the rate of thermolysis, or the rate of change of \( \alpha \) with time, \( t \), can be described by a temperature-dependant Arrhenius expression, \( k(T) \), scaled by a function \( f(\alpha) \), the conversion function:

\[ \frac{d\alpha}{dt} = f(\alpha) k(T). \] (2.3)

The conversion function reflects the mechanistic nature of the thermolysis process that is taking place. Assuming, crudely, that there is a single first-order reaction taking place at any particular temperature during the pyrolysis being studied, and which occurs uniformly throughout the biomass sample, this may be defined as:

\[ f(\alpha) = (1 - \alpha). \] (2.4)

The constant rate at which the sample is heated, \( \beta \), can simply be defined as the change of temperature, \( T \), with time, \( t \):

\[ \beta = \frac{dT}{dt}. \] (2.5)

Combining equations (2.3) and (2.4) gives:

\[ \frac{d\alpha}{dt} = \frac{1}{\beta} (1 - \alpha) k(T). \] (2.6)

Since the Arrhenius function \( k(T) \) has the form:

\[ k(T) = A \exp\left(\frac{-E_a}{RT}\right), \] (2.7)

it is possible to define:

\[ \frac{d\alpha}{dT} = \frac{1}{\beta} (1 - \alpha) A \exp\left(\frac{-E_a}{RT}\right). \] (2.8)

and thus the experimentally determined turning points of the DTG profile represent the maximum volatilization rates, i.e.:

\[ T = T_{max} \text{ when } \frac{d\alpha}{dT} = 0. \] (2.9)

Hence, by rearrangement the following expression is obtained:

\[ \ln \left( \frac{\beta}{T_{max}} \right) = \ln \left( \frac{RA}{E_a} \right) - \frac{E_a}{RT_{max}}. \] (2.10)

And so, from a graph of \( \ln(\beta/T_{max}) \) versus \( 1/T_{max} \), the values of \( E_a \) and \( A \) can be calculated [51].

2.4. Preparation of macroalgae (Laminaria digitata)

Samples of L. digitata were harvested from Marsden Bay, South Shields, UK (54°28′25.88″ N, 1°23′09.97″ W) on 28 October 2011 (figure 4). The samples were washed in distilled water to remove the majority of the sand and grit, and frozen at −18°C within 4 h of harvest. After being allowed to thaw naturally at room temperature for 8 h, the macroalgae were shredded, dried to a constant weight at 80°C, and ground and sieved to 250 μm. The dry, powdered macroalgae samples were either used immediately or returned to storage at −18°C.
2.5. Cu$^{2+}$ ion exchange in \textit{L. digitata}

The alkali and alkaline earth metals inherently present in a sample of wild \textit{L. digitata} were replaced with Cu$^{2+}$ ions via an ion-exchange process: the \textit{L. digitata} (as prepared in §2.4) were suspended in a solution of Cu(NO$_3$)$_2$ (100 ml, 1.0 M) and stirred vigorously for 6 h at room temperature. The ion-exchanged macroalgae were subsequently isolated by filtration, washed thoroughly with deionized water (100 ml) and dried to a constant weight at 80°C.

2.6. Thermal analysis of \textit{L. digitata}

Both the untreated \textit{L. digitata}, and the Cu$^{2+}$ ion-exchanged \textit{L. digitata} were dried overnight at 105°C immediately prior to analysis. TGA experiments were carried out on the dried, ground seaweed samples using a Perkin Elmer Pyris 1 analyser. Samples of 20.0 ± 0.5 mg were loaded into a platinum pan and spread evenly. The sample was subsequently heated from 25°C to 900°C at a heating rate (\(\beta\)) of 10°C min$^{-1}$ under a flow of dry N$_2$ at 25 ml min$^{-1}$. The first derivative of the TGA plot yielded the DTG profile.

DSC analyses were performed on a TA Instruments DSC analyser (Q1000, v. 9.9, build 303) by placing 5.0 ± 0.5 mg of sample into an aluminium pan, crimping it shut and then heating from 30 to 500°C at 10°C min$^{-1}$ under a flow of dry N$_2$ at 50 ml min$^{-1}$.

2.7. Elemental analyses

C, H and N compositions of all samples were determined by combustion on an Exeter Analytical CE440 elemental analyser by the Analytical Department of the Chemistry Department, Durham University.

The concentrations of 26 common metals in the \textit{L. digitata} (known to be present in significant concentrations from previous investigations [22,23]) were determined via inductively coupled plasma mass spectrometry analysis (ICP-MS) using a Thermo Fisher X–Series II analyser; the analysed samples were prepared by Carius tube digestion in a concentrated, ultrapure HNO$_3$:HCL mix (3:1 by volume). The Cu and Na concentrations in H-, Na- and Cu-Alg were also determined using this method. Fluka analytical TraceSELECT ultrapure acids and standards were used in the analyses and high-purity deionized water was used throughout.

3. Results and discussion

3.1. Pyrolysis of alginic acid and alginates

Samples of alginic acid (H-Alg), sodium alginate (Na-Alg) and copper(II) alginate (Cu-Alg) were prepared as in §2.1. Examination of their elemental analysis profiles (table 1) reveals that the exchange of sodium for copper ions occurred almost completely, with the equilibrium depicted in equation (2.1) lying predominantly to the right-hand side, an effect predicted in earlier studies on the affinity of alginates for Cu$^{2+}$ ions (see §1) [47,48].

A comparison was made of the pyrolysis behaviour of Cu-Alg against that of H-Alg and Na-Alg in order to probe the effect of the Cu$^{2+}$ ions in the alginate structure [36]. Broadly, it was found that for all three compounds, thermal degradation occurred in three discrete temperature windows (phases 1–3) defined by \(T_i\) (the onset of rapid pyrolysis) and \(T_f\) (the end of rapid pyrolysis). However, despite this apparent similarity, it was found that the behaviour of the different materials within these three temperature regimes varied dramatically, as demonstrated by the DTG (figure 5a) and TGA (figure 5b) curves. In particular, a detailed analysis of the three distinct pyrolysis regions highlights the dramatic influence exerted by the presence of the metal ions on the pyrolysis of the alginic acid polymer.

3.1.1. Phase 1: 25°C ≤ \(T < T_i\)

The small mass loss (around 5 wt%) observed in this region for H-, Na- and Cu-Alg is attributed to simple loss of moisture.
which had re-absorbed following drying to a constant weight at 105 °C prior to the TGA, consistent with the hygroscopic nature of these materials [24,28,52–54]. This is in agreement with the large endothermic peak during this temperature region on the DSC curve featured in figure 6, which results from water evaporating from the sample.

3.1.2. Phase 2: \( T_i \) to \( T_f \)

The region of the TGA profile that lies between \( T_i \) and \( T_f \) is arguably the most important when considering biomass pyrolysis in general (and that of related model materials) because it is within this window that the maximum degree of volatilization takes place, with between 40 and 50 wt% of the initial mass of the sample being lost. \( T_i \) corresponds to the temperature where rapid pyrolysis begins to take effect. With a heating rate, \( \beta \), of 10 °C min\(^{-1} \) under \( \text{N}_2 \), the value of \( T_i \) varies with Cu-Alg (150 °C) < H-Alg (161 °C) < Na-Alg (207 °C). During this period of rapid pyrolysis, several notable features appear at \( T_{\text{max}} \) (the temperature at which the maximum mass loss rate occurs) signified by an intense peak in the DTG curve. A summary of the values of \( T_i \), \( T_f \) and \( T_{\text{max}} \) for H-Alg, Na-Alg and Cu-Alg recorded at five different

Figure 5. The (a) DTG, (b) TGA and (c) degree of conversion profiles for the thermolysis of H-Alg, Na-Alg and Cu-Alg over the temperature range 25 – 1000 °C obtained with a heating rate (\( \beta \)) of 10 °C min\(^{-1} \) under \( \text{N}_2 \). Dashed line, Na; dotted line, Cu; solid line, H.
heating rates ($\beta$) is given in table 2. It can be seen that the H-Alg and Cu-Alg samples show two peaks ($T_{\text{max}1}$ and $T_{\text{max}2}$), whereas the Na-Alg only shows one (simply $T_{\text{max}}$); the latter represents a much greater rate of mass loss and occurs at a similar temperature to H-Alg $T_{\text{max}2}$. This indicates that the first step in the pyrolysis pathway is somehow inhibited (relative to H-Alg) by the Na$^+$ ions until some critical temperature (207°C), after which the subsequent reactions occur very rapidly. Many of the reactions that cause the rapid volatilization of the solid feedstock are not well understood and there is still much work to be done to gain a better understanding of this pyrolysis phase, both in the case of alginates and for biomass in general [55]. Interestingly, however, the DSC profiles for H-Alg, Na-Alg and Cu-Alg during this phase of pyrolysis (figure 6) all show sharp exothermic peaks, revealing that the net effect of the reactions that lead to the rapid volatilization stage is to release heat, presumably as more thermodynamically stable compounds are formed from the decomposition.

$T_f$ marks the end of the period of rapid volatilization and varies as Cu-Alg (270°C) < H-Alg (275°C) < Na-Alg (283°C); this is a much smaller temperature range than that for $T_e$ where approximately 60°C separates Cu-Alg from Na-Alg. This appears to be because the Na-Alg demonstrates a much higher mass loss rate during the period $T_i$ to $T_f$. Consequently, although the onset of rapid pyrolysis for Na-Alg begins at a higher temperature than for both Cu-Alg and H-Alg, volatilization of the sodium salt proceeds very quickly with mass loss ending at a temperature only slightly higher than those recorded for copper(II) alginate and alginic acid.

3.1.3. Phase 3: $T_f < T \leq 1000^\circ\text{C}$

The region from $T_f$ onwards is generally regarded as being a period of slower, sustained degradation in biomass pyrolysis. Reaction processes occurring within this region are thought to consist mainly of secondary pyrolysis reactions, tar
cracking, char formation and the degradation of thermally robust inorganic constituents [24,28,52–54]. Consequently, the rate of mass loss is considerably lower than that in phase 2, with the final mass achieved corresponding to the amount of char produced.

For biomass such as macroalgae, the residual char is primarily composed of carbon and inorganic materials, such as metal oxides and metal carbonates, which form as the metal ions bound to the alginites react with the organic matrix upon degradation [44]. Some of the inorganic salts may be products of secondary reactions, such as the formation of metal carbonates from the reaction between CO₂ (released throughout the pyrolysis process) and other metal oxides. To survive to the char stage, however, the inorganic constituents need to be thermally robust, and some may degrade prior to 1000°C. Figure 7 shows the TGA/DTG profiles of some of the inorganic constituents (namely copper, sodium and calcium carbonate) that may be expected to form during the pyrolysis of the Na-Alg and Cu-Alg. CuCO₃ degrades to CuO and CO₂ at around 300°C (with a later, much smaller mass loss at around 900°C, as the CuO begins to form Cu₂O [56]; figure 7). Consequently, no peak is seen that corresponds to the degradation of CuCO₃ in the pyrolysis of Cu-Alg between Tf and 1000°C. Conversely, pure Na₂CO₃, which melts at around 850°C, does not start to significantly volatilize until temperatures above 1000°C [57] and hence no features arising from this material were observed. However, a high temperature thermal decomposition feature is apparent during the pyrolysis of Na-Alg, something that has been attributed to small quantities of calcium ion impurities present in the alginate that initially react to form CaCO₃ [44], and which subsequently decomposes at temperatures around 700°C (figure 7) [58]. The H-Alg material contains only trace inorganic content and is virtually completely degraded by 650°C. Thus, in the higher temperature regions (more than 650°C), there are no regions of significant mass loss in the TGA profile that correspond to the degradation of inorganic salts.

As expected, the inorganic materials present in the Cu-Alg and Na-Alg materials are not fully volatilized by 1000°C. Metal oxides that form during pyrolysis such as Cu₂O, CuO and Na₂O remain intact, something that results in higher char yield for the Cu-Alg and Na-Alg samples (14.6 and 17.0 wt%, respectively), compared with that from H-Alg (1.1 wt%) [12]. Consequently, by using TGA data directly, it is difficult to compare the effects of metals in the thermal degradation of metal-rich biomass samples, as the relative mass loss is smaller as a result of the significant amounts of inorganic char formed. Thus, to gain a deeper insight into the rate of volatilization of the important organic
constituents of the biomass occurring during pyrolysis, a plot of the degree of conversion \( \alpha \) (defined in equation 2.2) against temperature, as depicted in figure 5c, can be informative. This degree of conversion \( \alpha \) does not include the amount of residual char and only considers matter that is volatilizable below the maximum temperature used in the experiment, 1000°C. Consequently, samples such as Cu-Alg and Na-Alg, which have comparably high inorganic content (with 10–15 wt% consisting of metal ions), can be compared directly with H-Alg, which is almost entirely organic. Thus, whereas the TGA profiles suggest that the extent of mass loss of Na-Alg with temperature is consistently lower than for H-Alg, when the mass lost is considered as a fraction of the total amount volatilized (i.e. the degree of conversion), it can be seen that there is a period between 240°C and 330°C where the Na-Alg has lost a greater proportion of its volatilizable mass than has H-Alg, indicating that the Na\(^+\) ions promote pyrolysis between these temperatures.

Furthermore, the TGA data suggest that the H-Alg and Cu-Alg materials are comparable in terms of the extent of mass lost upon pyrolysis to 285°C. However, if the degree of conversion data \( \alpha \) are examined, it becomes apparent that the samples of H-Alg and Cu-Alg do not achieve the same value until a pyrolysis temperature of 480°C. This latter observation indicates that the Cu\(^{2+}\) ions promote pyrolysis of the organic matter over a much wider temperature range than would be apparent from the TGA profile alone. Indeed, the data presented in figure 5c also clearly demonstrate that the presence of Cu\(^{2+}\) ions inhibits the later stages (phase 3) of alginic acid pyrolysis quite considerably (cf. H-Alg and Na-Alg) and severely slows down the rate of volatilization above approximately 500°C.

This observation contradicts previous studies, where the presence of mono- (Na\(^+\)) and divalent (Ca\(^{2+}\), Co\(^{2+}\)) metal ions have all been shown to inhibit the onset of pyrolysis of alginates relative to that of the parent acid [43,44]. By contrast, the results presented here indicate that Cu\(^{2+}\) ions clearly shift the onset of pyrolysis to a lower temperature.
with respect to the (practically) metal-free alginic acid. To explain this phenomenon, however, requires a better understanding of the interaction of the metal ions with both the mannuronic and guluronic acid residues that comprise the alginates as it appears that, though the alginic acid shows a high affinity for Cu$^{2+}$ ions, the presence of such ions also serves to destabilize the polymer at higher temperatures. In order to better quantify the observed trend in thermal stability (i.e. Cu-Alg, H-Alg, Na-Alg) a kinetic study was carried out for the second stage of pyrolysis for all three compounds. The mathematical details of the model used are elaborated in §2.3, but the principle behind the analysis was to plot ln($\beta/T_{\text{max}}^2$) versus $1/T_{\text{max}}$, where $T_{\text{max}}$ represents a point of maximum mass loss rate (identified as a turning point in the DTG profile) for five different heating rates ($\beta$ = 5, 10, 20, 30 and 40 °C min$^{-1}$).

From this plot (figure 8), the gradient can be used to extract the energy of activation, $E_a$, for the reaction(s) occurring at that point in the pyrolysis, with the intercept giving the pre-exponential factor, $A$. The plots in figure 9 show the

![Figure 9. The DTG profiles for the main pyrolysis region of (a) H-Alg, (b) Cu-Alg and (c) Na-Alg at heating rates ($\beta$) of 5, 10, 20, 30 and 40 °C min$^{-1}$ under N$_2$.](http://rsfs.royalsocietypublishing.org/Downloaded from http://rsfs.royalsocietypublishing.org/10.1098/rsfsi.2012.0046)
DTG profiles at the five different heating rates (β). As β increases, the DTG curve maintains a similar shape, but is shifted to a higher temperature; this is a well-documented effect that arises owing to the delay in heat transfer to the samples being analysed [59]. The results of the kinetic analyses are summarized in table 2. The energy of activation, $E_a$ was calculated for two points in the pyrolysis ($T_{\text{max}1}$ and $T_{\text{max}2}$) for H-Alg and Cu-Alg, and at one point ($T_{\text{max}1}$) for Na-Alg obtained from the peaks in the DTG profiles (figure 5a). The values of $E_a$ give an indication of the energy required to initiate the reaction(s) occurring at that temperature in the pyrolysis, and so they provide a useful comparison of the ease of volatilization of the compounds relative to each other. It is unsurprising then that the trends in the values of $E_a$ reflect the trends in the values of $T_{\text{f}}$ ($T_{\text{f}}(\text{Cu-Alg}) < T_{\text{f}}(\text{H-Alg})$), thus $E_a(T_{\text{max}1}\text{Cu-Alg}) < E_a(T_{\text{max}1}\text{H-Alg})$ and $E_a(T_{\text{max}2}\text{Cu-Alg}) < E_a(T_{\text{max}2}\text{H-Alg})$ and thus the kinetic data further corroborate the observation that Cu$^{2+}$ ions promote volatilization in the rapid pyrolysis phase with respect to H-Alg. Further comparison with Na-Alg is not straightforward however, as the DTG profiles (figure 9c) are not well resolved. Consequently, only one value of $T_{\text{max}}$ (and thus $E_a$) can be determined for Na-Alg (table 2) from the single, broad peak, which is clearly associated with a larger number of reactions than the separate, narrower peaks in the Cu-Alg and H-Alg spectra. This gives rise to the correspondingly large value of $E_a$ for sodium alginate, which cannot meaningfully be correlated with the values of $E_a$ determined for the other compounds.

Finally, coupled TGA-FTIR analysis gives insight into aspects of the thermal degradation pathways of H-Alg, Na-Alg and Cu-Alg, and the differences between them. Figure 10 shows that the primary volatile component product for this ‘slow’ pyrolysis, in all three cases, is CO$_2$, as evidenced by the intense absorbance at 2360 cm$^{-1}$; this observation has been reported previously from studies using coupled TGA–gas chromatography/mass spectrometry (Py-GC-MS) [42,44]. Interestingly, if the intensity of the IR absorbance at 2360 cm$^{-1}$ is plotted against temperature during the pyrolysis of H-Alg, Na-Alg and Cu-Alg over the temperature range 150–300°C (figure 11a), the trace can be seen to completely replicate the trend in mass loss shown in the equivalent section of the TGA curve (figure 11b). Thus, it is possible that the rapid period of pyrolysis that begins at $T_{\text{f}}$ (discussed above) is most likely attributable to decarboxylation of the carboxylate group of the alginites, which explains the rapid release of CO$_2$.

Beyond the temperature region 150–300°C, the amount of CO$_2$ evolved is seen to increase to a maximum in the case of Cu-Alg and H-Alg, but decrease in the case of Na-Alg. This decrease is a consequence of the reaction between CO$_2$ and sodium salts such as Na$_2$O, from which Na$_2$CO$_3$ can form, thus retaining the CO$_2$ until decomposition at much higher temperatures (figure 11c) [44]. Of course, the formation of carbonates is not possible in the case of the Cu-Alg (because CuCO$_3$ is not stable at these temperatures; figure 7), and for H-Alg, which does not contain significant metallic species for carbonates to form. The amount of CO$_2$ released is highest in H-Alg (as evidenced by the larger area under the curve in figure 11c), which is expected owing to the higher carbon content of the starting material compared with the metal salts.

Other minor peaks in the TGA-FTIR profile indicate that a number of other compounds may be evolved in the pyrolysis processes. Earlier studies have suggested that the minor peaks observed between 1500 and 1800 cm$^{-1}$ in the IR spectrum that begin to appear after around 300°C (absorbance around 0.02) could be due to a mixture of small, volatile, organic molecules bearing carbonyl groups such as formaldehyde, acetone and furfural, among others [42,44].

### 3.2. Influence of metals on the pyrolysis of macroalgae

In order to test the applicability of the results from the study of model biomass compounds (H-Alg, Na-Alg, Cu-Alg) described in §3.1, whereby Cu$^{2+}$ ions were shown to promote the onset of pyrolysis of alginic acid, an actual sample of macroalgal biomass should be subject to thermal degradation to test for similar effects. Indeed, previous studies have examined the role of metals in macroalgal pyrolysis by removing them completely and analysing the metal-stripped materials. However, this approach requires the macroalgae to be treated via washing with acid, something that has the additional
with a heating rate ($\beta$) of 10°C min$^{-1}$ under $N_2$. (b) TGA profile for the thermolysis of Na-Alg, Cu-Alg and H-Alg over the temperature range 150–300°C obtained with a heating rate ($\beta$) of 10°C min$^{-1}$ under $N_2$. (c) Plot of absorbance at 2360 cm$^{-1}$ versus temperature for the thermolysis of Na-Alg, Cu-Alg and H-Alg over the temperature range 25–1000°C obtained with a heating rate ($\beta$) of 10°C min$^{-1}$ under $N_2$. Dashed line, Na; dotted line, Cu; solid line, H.

**Figure 11.** (a) Plot of absorbance at 2360 cm$^{-1}$ versus temperature for the thermolysis of Na-Alg, Cu-Alg and H-Alg over the temperature range 150–300°C obtained with a heating rate ($\beta$) of 10°C min$^{-1}$ under $N_2$. (b) TGA profile for the thermolysis of Na-Alg, Cu-Alg and H-Alg over the temperature range 150–300°C obtained with a heating rate ($\beta$) of 10°C min$^{-1}$ under $N_2$. (c) Plot of absorbance at 2360 cm$^{-1}$ versus temperature for the thermolysis of Na-Alg, Cu-Alg and H-Alg over the temperature range 25–1000°C obtained with a heating rate ($\beta$) of 10°C min$^{-1}$ under $N_2$. Dashed line, Na; dotted line, Cu; solid line, H.

The detrimental effect of removing a significant fraction of the soluble organic constituents such as mannitol and fucose and potentially hydrolysing some of the carbohydrates [31,32]. Consequently, it is very difficult to determine which effects upon the pyrolysis are due to the presence or absence of the metals, and which result from the removal of the soluble biomolecules. Here, we present a different and novel approach whereby instead of removing the metals, samples of seaweed are saturated with one particular metal species (in this case copper) to determine the effects on pyrolysis with minimal alteration to the volatilizable organic matter. This methodology is especially suited to the study of brown macroalgae, which have an extremely high affinity for Cu$^{2+}$ ions, making it possible to achieve very high levels of ion exchange with relative ease [48].

To this end, a sample of wild *L. digitata* was subject to a metal ion exchange process, which resulted in replacement of around 93 per cent of the alkali, alkaline earth and other trace metals by Cu$^{2+}$ ions. Table 3 depicts the elemental compositions of the *L. digitata* samples pre- and post-impregnation via ion exchange. It was found that the original seaweed, as collected, contained around 122 000 (±1000) mg metal/kg dry seaweed, which was increased to 161 000 (±1000) mg metal/kg dry seaweed after copper-ion exchange, accompanied by a slight decrease in carbon content (2.0 wt%). The data reported in table 3 also suggest that, within experimental uncertainty, electroneutrality of the seaweed was maintained according to equation (2.1). Furthermore, the low nitrate content of the ion-exchanged material indicates that the copper detected was bound to the biomass and not residual Cu(NO$_3$)$_2$ used for impregnation, which was removed during the washing stages.

The two samples of *L. digitata* (the unadulterated sample and its Cu-exchanged counterpart) were pyrolysed under the same experimental conditions as described earlier for H$_2$, Na- and Cu-Alg; the results are shown in the TGA/DTG plots in figure 12. Generally speaking, these analyses reveal that the Cu-doped macroalgae sample shows the same mass loss regions as the H$_2$, Na- and Cu-Alg samples; dehydration, rapid pyrolysis and slow degradation phases are readily identifiable. Notably, although the onset of rapid pyrolysis occurs at a higher temperature for the real macroalgae biomass samples relative to those of the model compounds, the Cu$^{2+}$ ions are seen to exert a similar influence and Cu-doped macroalgae ($T_i = 164°C$) are observed to begin rapid pyrolysis at a lower temperature compared with the unadulterated macroalgae ($T_i = 180°C$). The same trend is also true for the values of $T_{\text{max}}$ ($T_{\text{max}}$(Cu(II)-L.dig) = 236°C compared with $T_{\text{max}}$(L.dig) = 254°C). However, at $T_f$, the two seaweed samples begin to show remarkably similar mass loss profiles, something that continues until around 650°C, where the unadulterated macroalgae show a very slight additional mass loss relative to the Cu-exchanged. This latter mass loss is most likely to be a result of thermolysis of CaCO$_3$ (as shown by the data presented in figure 7), which forms owing to the sizeable concentration of Ca$^{2+}$ present in the biomass (2.5 wt%). Thus, the conclusions drawn from the kinetic studies on the model alginate compounds are also true in the case of actual macroalgal biomass: the presence of Cu$^{2+}$ ions promotes pyrolysis at lower temperatures, but does not assist in the later stages of high temperature volatilization.

The similarities between the thermal behaviour of the model compound (copper(II) alginate) and the real biomass (copper(II)-doped *L. digitata*) can be further demonstrated by reference to the DSC profiles (figure 13e). These analyses show that, broadly, the major exotherms for the Cu-Alg overlap with those of the copper(II)-doped *L. digitata*, with the peaks in the heat flow to the latter material being less pronounced owing to the presence of other (thermally stable)
Table 3. Partial elemental profile of unadulterated *L. digitata* and *L. digitata* treated in a solution of Cu(II) ions

| Element | Cr | Ba | Li | Mn | Fe | Ni | Zn | Rb | Mo | Ag | Pb | Na | Mg | K | Ca | Sr | Cu | Total |
|---------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|-----|-------|
| Amount (mg/kg seaweed) | 0.04 | 0.10 | 0.14 | 0.07 | 2.07 | 0.02 | 0.80 | 0.11 | 0.01 | 1837 | 556 | 12.8 | 1020 | 625 | 19.6 | 0.05 |
| Charge | 2+ | 2+ | 1+ | 2+ | 2+ | 2+ | 2+ | 1+ | 2+ | 2+ | 2+ | 2+ | 2+ | 2+ | 2+ | 2+ | 1+ | 5+ | 0.6 |
| Concentration (mmol/kg seaweed) | 4075 | 3 | 122 | 677 | 322 | 677 | 21 | 4 | 141 | 1 | 6 | 15 | 2 | 9 | 0 | 2 | 172 | 3 |
| Amount (mg/kg seaweed) | 0.04 | 0.10 | 0.14 | 0.07 | 2.07 | 0.02 | 0.80 | 0.11 | 0.01 | 1837 | 556 | 12.8 | 1020 | 625 | 19.6 | 0.05 |
| Charge | 2+ | 2+ | 1+ | 2+ | 2+ | 2+ | 2+ | 1+ | 2+ | 2+ | 2+ | 2+ | 2+ | 2+ | 2+ | 2+ | 1+ | 5+ | 0.6 |
| Concentration (mmol/kg seaweed) | 4075 | 3 | 122 | 677 | 322 | 677 | 21 | 4 | 141 | 1 | 6 | 15 | 2 | 9 | 0 | 2 | 172 | 3 |

aOn a dry basis.
bBe, Co, Ga, Cd, Cs, Bi, Tl and V were also detected but below milligram per kilogram levels.
cThe sum of the number of moles of each element multiplied by its charge.

Thus the requirement to make comparative studies with model compounds is very relevant, as they can help to

4. Conclusions and outlook

The complex nature of the thermal behaviour of seaweeds demonstrated throughout this study indicates that their thermolysis pathways are not straightforward and that the TGA and DSC profiles encompass a myriad of diverse reactions. Thus the requirement to make comparative studies with model compounds is very relevant, as they can help to
Figure 12. The (a) DTG and (b) TGA profiles for the thermolysis of raw *L. digitata* and *L. digitata* treated in a solution of Cu$^{2+}$ ions in the range 25–800°C with a heating rate (β) of 10°C min$^{-1}$ under N$_2$. Solid line, copper(II)-doped *L. digitata*; dashed line, *L. digitata*.

Figure 13. (a) Comparison of DSC curves for copper(II) alginate (solid line) and copper(II)-doped *L. digitata* (dotted line) over the temperature range 50–400°C obtained with a heating rate (β) of 10°C min$^{-1}$ under N$_2$. (b) Comparison of DSC curves for unadulterated *L. digitata* (solid line) and copper(II)-doped *L. digitata* (dotted line) over the temperature range 50–400°C obtained with a heating rate (β) of 10°C min$^{-1}$ under N$_2$. 
pinpoint the important factors necessary for the study of biomass pyrolysis without the complication of sample heterogeneity. In this respect, copper(II) alginate was found to be a convincing compound with which to model the effects of Cu2⁺ ions on a sample of brown macroalgae. Consequently, though only samples of *L. digitata* were examined, the agreement between the model study and the study using whole biomass suggests that the findings in this paper should be applicable to most brown (alginate-containing) macroalgae.

Here, Cu2⁺ ions have been found to have a dramatic impact on the thermal stability of polymeric alginic acid, promoting the onset of pyrolysis where other mono- and divalent cations have been found to inhibit it. This effect is evidenced by a reduction in temperature of the onset of rapid pyrolysis of copper(II) alginate compared with the parent alginic acid that, as might be expected, is also accompanied by a lowering of the activation energies at various points in the conversion pathway. It is not accurate, however, to describe the copper as acting catalytically towards the pyrolysis of the alginic acid as, at elevated temperatures (more than 500°C), the Cu2⁺ ions clearly begin to inhibit conversion of the solid into volatile compounds. Indeed, with such a multitude of reactions taking place over the course of the pyrolysis process, the exact role of the copper is difficult to discern, but it clearly appears to destabilize the alginic polymer and, consequently, is beneficial during the early stages of pyrolysis, the region that is of most importance in the production of biofuels and chemicals.

Given the high affinity of alginates and, consequently, macroalgae for Cu2⁺ ions, it is anticipated that other samples of brown seaweed grown in or around copper-contaminated wastewater streams will demonstrate effects similar to those described above. This highlights the importance of establishing the metal profile of a sample of macroalgae prior to analysis, especially in the case of comparative studies, such as those that compare different species or the effects of different catalysts. It is likely that a greater understanding of the destabilizing effects of Cu2⁺ ions reported in this paper will be accompanied by a better understanding of the interaction of seaweed biomass with metal ions as a whole, which in turn opens the way to better utilization of macroalgae as a resource.

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