Thermochemical Fuel Behaviour of Micro- and Macroalgal Biomass

Daniel James Lane

Thesis submitted for the degree of Doctor of Philosophy

School of Chemical Engineering

The University of Adelaide, Australia

October 2015

Declaration

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Abstract

Algal biomass has gained recent interest as an energy source due to diminishing reserves of fossil fuels and growing pressure to reduce emissions of greenhouse gases. The most developed technologies for converting biomass to energy and fuels are based on thermochemical processes, particularly pyrolysis, combustion, and gasification. However, little is known about the behaviour of micro- and macroalgae in these processes. The aim of this thesis was to characterise the thermochemical fuel behaviour of micro- and macroalgal biomass, with emphasis on the following areas of fuel particle conversion: char reactivity; oxidation of carbon; conversion of fuel-N; occurrence of the inorganic elements; bed agglomeration; release of volatile inorganic elements; and mobilisation of trace elements. A range of laboratory-scale experiments was carried out in order to address each of these areas.

Char reactivity was characterised by gasifying four samples of algae in a thermobalance in pure CO_2 at 850 °C, following *in situ* drying and devolatilisation of the algal samples. The reactivity of the chars varied for different species of algae and for different cultivation regimes. The oxidation of carbon and conversion of fuel-N to NO were studied by monitoring the concentrations of gas phase species released during fixed-bed combustion. Conversions of C to CO and CO_2 exceeded 84% for all of the tested algae. In most cases, a greater proportion of the total C was released during devolatilisation rather than during char oxidation, which is consistent with the high volatile matter contents reported in the literature for algal biomass fuels. The total conversion of fuel-N to NO ranged between 6 – 21g of N / 100g of fuel-N and was found to diminish with increasing fuel-N content. In most cases, emissions of NO were predominately released during devolatilisation. These results provide a basis for the development of control measures needed to minimise emissions of NO in combustion processes. The char reactivity measurements and partitioning of released C between volatiles and char, collectively enable improved predictions of the extent of carbon burnout in industrial-scale thermochemical processes.

The occurrence of the main inorganic elements in algal biomass was studied by means of chemical fractionation. Scanning electron microscopy and X-ray diffraction analyses were used to aid interpretation of the results. The relative proportions and speciation of the main inorganic elements were largely dependent on the cultivation regime. A high

level of inorganic, water-soluble, alkali salts was found in all of the tested algae. These salts are likely to cause operational problems in industrial reactors such as fouling, ash deposition, corrosion, and in the case of fluidised-bed technologies, bed agglomeration. In order to gain insights into bed agglomeration, interactions between algal ashes and quartz bed material were simulated by heating pellets consisting of algal ashes mixed with quartz particles in a muffle furnace at 850 °C in air. Analysis of cross-sections of the resultant pellets indicated that bed agglomeration follows a non-reactive mechanism, involving the binding of bed particles with an ash-derived melt. Based on this outcome, it is expected that bed agglomeration will be largely controlled by the formation of molten ash on inert bed particles during combustion, rather than the ash reacting with the bed particles.

The release of Cl, S, P, K, and Na was characterised by preparing char and ash samples in a fixed-bed reactor, at a range of temperatures (500 – 1100 °C) and under different gas atmospheres (N_2, 2% O_2, and CO_2) relevant to pyrolysis, combustion and gasification processes. The extent to which these elements volatilise was determined for different species of algae by means of mass balances based on elemental analyses of the char and ash residues. Results for the different species of algae were compared and explained in terms of mechanisms existing for coal and terrestrial biomass fuels. Differences in the volatile behaviour of Cl, S, K, and Na were significant between marine and freshwater species but were only minor between micro- and macroalgal species. The volatile behaviour of P was similar for all of the tested algae. If volatilised, the studied inorganic elements may cause fouling, ash deposition, and corrosion. The results from this study therefore provide essential knowledge for the prediction and mitigation of these problems.

The potential for mobilisation of 11 environmentally important trace elements (As, Be, Co, Cu, Mn, Ni, Pb, Sb, Se, V, Zn) was assessed during the thermal conversion of two samples of algae which had been cultivated in ash-dam water at a coal-fired power station. The volatility of the trace elements was studied in the same experimental setup as that used to study the volatility of Cl, S, P, K, and Na. Se and As were substantially volatilised at low temperatures (<500 °C), under pyrolysis, combustion, and gasification gas atmospheres. Zn, Pb, and Sb were also substantially volatilised, but at higher temperatures (700 – 1000 °C). Batch leaching tests were carried out in order to assess the stability of the trace elements in the char and ash residues. The trace elements were

generally more stable following thermal conversion with the exception of V, which was up to 4 – 5 times more leachable in the combustion ashes than in the corresponding algal feedstock. The trace elements were generally more stable in residues prepared under pyrolysis and gasification conditions than in residues prepared under combustion conditions. The results from this study show that several trace elements have potential to be released into the environment in significant quantities when ash-dam cultivated algae are thermally processed. Appropriate control measures would need to be implemented to minimise the release of these elements in industrial-scale thermochemical processes.

The outcomes of this thesis collectively provide an improved understanding of the potential for operational and environmental problems associated with the thermochemical conversion of micro- and macroalgal biomass. This will help in the development of commercial processes for the utilisation of these resources.

Acknowledgements

I am grateful for the support of the Australian Research Council (ARC) and industry partner SQC Pty. Ltd. for being the primary funders of this work. I also wish to acknowledge the Australian Renewable Energy Agency (ARENA), the Advanced Manufacturing Cooperative Research Centre (AMCRC), and the National Technology Agency of Finland (TEKES), for their contributions.

I would like to express my gratitude to my research supervisors, Prof. Peter Ashman, Associate Prof. David Lewis, and Dr. Philip van Eyk. I thank Peter, for sharing his expert advice with me and for overseeing this project from start to finish. I thank David, for introducing me to the world of algae and for the countless opportunities that he has provided for me over the last few years. I thank Philip, for all of his support, both in and out of the laboratory. His guidance has been invaluable to me.

I thank my Finnish collaborators, Prof. Mikko Hupa and Dr. Maria Zevenhoven, for giving me the opportunity to join their research group at Åbo Akademi in 2013. I will not forget their warm hospitality and the friends that I made while visiting their group. I would also like to acknowledge my collaborators from James Cook University in Queensland, particularly Prof. Rocky de Nys, Dr. David Roberts, and Dr. Andrew Cole, for growing biomass for my experiments and for their valuable advice during the drafting of paper manuscripts.

I am indebted to the staff of the Chemical Engineering workshop, Jason Peak, Mike Jung, and Jeff Horns, for their tremendous assistance during the experimental campaign of this project. I am also indebted to Sue Earle, Monica Dinan, and Debra Percey, for lightening my administrative load. I thank my fellow researchers for hearing out my ideas over coffee breaks, particularly Mason Erkelens, Steve Amos, Anne Philcox, Quang Doan, Mike Jureidini, Peijun Guo, Xue Dong, and Youjian Zhu.

Finally, I would like to thank my family, John, Jo, Tessa, and David, for their life-time of support and encouragement.

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Preface

Most of the work presented in this thesis was carried out within the School of Chemical Engineering at the University of Adelaide between 2012 and 2015. Additionally, part of the work was carried out within the Process Chemistry Centre at Åbo Akademi University in Turku, Finland in 2013. The four following journal papers contain the main body of work of this thesis:

Paper I	Lane DJ, Ashman PJ, Zevenhoven M, Hupa M, van Eyk PJ, de Nys R, Karlström O, Lewis DM. Combustion behavior of algal biomass: carbon release, nitrogen release, and char reactivity. Energy & Fuels 2014; 28 (1): 41-51.
Paper II	Lane DJ, Zevenhoven M, Ashman PJ, van Eyk PJ, Hupa M, de Nys R, Lewis DM. Algal biomass: occurrence of the main inorganic elements and simulation of ash interactions with bed material. Energy & Fuels 2014; 28 (7): 4622-4632.
Paper III	Lane DJ, van Eyk PJ, Ashman PJ, Kwong CW, de Nys R, Roberts DA, Cole AJ, Lewis DM. Release of Cl, S, P, K, and Na during thermal conversion of algal biomass. Energy & Fuels 2015; 29 (4): 2542-2554.
Paper IV	Lane DJ, van Eyk PJ, de Nys R, Roberts DA, Cole AJ, Ashman PJ. Mobilisation of trace elements during thermal conversion of algae cultivated in ash dam water. Biomass & Bioenergy 2015; 83: 183–195.

Chapter 1

Introduction

1. Introduction

1.1. Background

Growing pressure to establish fuel security and ongoing global warming have brought recent attention to renewable sources of energy. Biomass is currently the most used source of renewable energy and its use is projected to continue to displace that of non-renewable fossil fuels in the future [1]. There are many environmental advantages to be gained from substituting fossil fuels for biomass, such as reduced net levels of greenhouse gas emissions. Technologies based on thermochemical processes, particularly pyrolysis, combustion and gasification, have long been used to convert biomass to energy and fuels, and are relatively well established when compared with technologies based on biochemical and solvent extraction processes. However, the types of biomass used in these processes today (*e.g.* wood and dedicated energy crops) are limited in availability and there are sustainability issues associated with their production on an industrial scale [2]. This has motivated research into the utilisation of various "new" sources of biomass in these thermochemical processes.

Both micro- and macroalgae are currently underutilised biomass resources which have several advantages as an energy source. The production of algae has excellent potential for high areal energy yields, with productivities as high as 70 dry tonnes ha^{-1} $year^{-1}$ commonly reported in the literature [3]. This value compares favourably to values typically reported for wood (5 – 15 dry tonnes ha^{-1} $year^{-1}$) and for dedicated energy crops (8 – 30 dry tonnes ha^{-1} $year^{-1}$) [4, 5]. The cultivation of algae can be carried out in both freshwater and seawater based production systems [6]. These systems can be situated on non-arable land [7], which limits direct competition with the production of food crops, a major drawback to the production of biomass fuels of terrestrial origin [2]. Algae can also be cultivated in various types of contaminated wastewater [8]. This opens up opportunities for combining the production of energy and fuels with bioremediation.

A significant amount of work has gone into developing industrial-scale processes for the commercial production of algal biomass [6, 7, 9]. Comparatively little is known about the behaviour of the produced biomass in thermochemical processes. Previous studies in this field have mainly focused on a limited range of standard fuel analyses,

which are typically performed as a first step when characterising new fuels. These studies have shown the chemical composition of algae to differ in many ways from that of commonly used solid fuels such as coal and wood. When compared with these fuels both micro- and macroalgae generally contain higher levels of impurities, such as N, S, Cl, P, K, Na, and a variety of trace metals and metalloids. Many of these impurities are capable of forming harmful pollutants during thermal conversion [10] or are intimately connected with major operational problems such as fouling, ash deposition, corrosion and bed agglomeration [11, 12]. In order to accurately assess the potential for environmental and operational problems during the thermal conversion of micro- and macroalgal biomass fuels, further studies, which address the behaviour of these impurities in thermochemical processes, are needed.

The principal aim of this study is to characterise the thermochemical fuel behaviour of micro- and macroalgal biomass. This thesis will primarily focus on areas of fuel behaviour which are of importance to operational and environmental problems in industrial-scale thermochemical processes. The detailed objectives of this thesis are outlined in Section 2.9.

1.2. Scope and structure of thesis

Chapter 2 provides a critical review of the literature on the thermochemical fuel behaviour of micro- and macroalgal biomass. The emphasis of the review is on the following areas of fuel particle conversion: char reactivity; oxidation of carbon; conversion of fuel-N; occurrence of the inorganic elements; bed agglomeration; release of volatile inorganic elements; and mobilisation of trace elements. The review encompasses relevant literature on conventional solid fuels such as coal and wood, however, primarily focuses on literature which deals specifically with algal biomass fuels. Limitations in the literature are established at the end of the review. These limitations determined the direction of the work presented in the proceeding chapters.

Chapter 3 examines the conversion of fuel-N to NO and the oxidation of fuel-C to CO and CO_2 during the combustion of micro- and macroalgal biomass. The chapter also examines the gasification reactivities of chars produced from different species of algae.

Chapter 4 consists of two parts. The first part examines the occurrence, particularly the speciation, of the main inorganic elements in micro- and macroalgal biomass. The

second part examines the interactions that take place between algal ashes and quartz bed material under conditions relevant to fluidised-bed combustion.

Chapter 5 investigates the extent to which five volatile inorganic elements (Cl, S, P, K, and Na) are released in pyrolysis, combustion, and gasification processes. The release of these elements is explained in terms of existing mechanisms, which have been proposed by previous authors for coal and terrestrial biomass fuels.

Chapter 6 examines the mobilisation of 11 trace elements (As, Be, Co, Cu, Mn, Ni, Pb, Sb, Se, V, Zn) during pyrolysis, combustion, and gasification of ash-dam cultivated algae. The volatility of the TEs is assessed under different gas atmospheres (N_2, 2% O_2, CO_2), and at different temperatures within the range 500 - 1100 °C. The resultant leachability of the trace elements in the char and ash residues is also assessed.

Chapter 7 presents the conclusions from the body of work and recommendations for future work in the field.

References cited in Chapters 1, 2, and 7 are listed at the end of the thesis. References cited in Chapters 3 - 6 are provided within the chapters themselves.

Chapter 2

Literature Review

2. Literature review

2.1. Introduction

This chapter presents a critical review of the literature on the thermochemical fuel behaviour of micro- and macroalgal biomass. The following areas are addressed in the review:

- Oxidation of carbon and char reactivity
- Conversion of fuel-N
- Occurrence of the inorganic elements
- Bed agglomeration
- Release of volatile inorganic elements
- Mobilisation of trace elements

Greater emphasis has been given to literature which deals specifically with algal biomass fuels. However, most of the knowledge in the aforementioned areas is largely rooted in studies based on coal and terrestrial forms of biomass, such as wood. For this reason, relevant literature on these fuels is also included in the review.

2.2. Algal biomass

Algae constitute a diverse group of photosynthetic organisms which are categorised into two sub-groups, microalgae and macroalgae, based on their size. Microalgae include both unicellular and simple multi-cellular algae [13] which range from less than one micrometre to a few hundred micrometres in size [14]. Macroalgae range from around 1mm to up to 60 m in size [15] and are extremely diverse in structure. It is estimated that somewhere between 36,000 and 10 million species of algae exist worldwide [14], however only a select few species have been studied for energy-related applications. The production of micro- and macroalgal biomass for energy applications generally involves the following stages: cultivation, harvesting, and drying (or dewatering) [7, 9]. The thermochemical fuel properties of the produced algal biomass depend not only on species selection but also on the processing history in each of these production stages, particularly cultivation.

2.3. Standard fuel analyses

A standardised group of analyses is generally carried out as a first step when characterising new fuels. These analyses include proximate, ultimate, heating value, and elemental analyses. They each provide initial indications of different aspects of pyrolysis, combustion, and gasification behaviour.

The proximate analysis divides the fuel into four separate constituents (moisture, volatile matter, fixed carbon, and ash) which are based on the phases of fuel particle burnout. When a solid fuel particle is first introduced to a reactor, fuel moisture is evaporated. Fuel moisture includes water which can be evaporated from the fuel by drying at low temperatures (~100 °C) but does not include water molecules which are chemically bound to the fuel. As the fuel particle continues to heat to higher temperatures, the fuel particle undergoes devolatilisation, which involves rapid release of volatile components in the organic matrix (volatile matter). The organic matter remaining after devolatilisation is termed fixed carbon. In combustion and gasification processes the fixed carbon is converted by heterogeneous reactions with gas phase reactants. The residual inorganic material remaining at the end of the combustion or gasification process is the ash. The partitioning of a fuel into its proximate constituents provides vital information regarding reactor availability and is used to gain an initial indication of the expected quantities in both gas and solid phase product streams.

The ultimate analysis shows the total concentrations of C, H, N, O, and S in the fuel, on a dry or dry and ash-free basis, and provides an initial indication of emissions. Heating value is a measure of the energy content of the fuel and provides an upper limit to the energy released during combustion. The elemental analysis shows the concentrations of the inorganic elements in the fuel or in the ash. The major (>1% w/w) and minor (0.1 - 1% w/w) inorganic elements largely determine the properties of the ash (or char) formed in thermochemical processes. Knowledge of their concentrations is essential for the prediction and mitigation of operational problems in industrial-scale reactors. Many of the trace (<0.1% w/w) inorganic elements are capable of forming harmful pollutants which are toxic at low concentrations. Knowledge of the concentrations of the trace elements (TEs) is therefore important from an environmental aspect.

Standard fuel analyses have been reported in the literature for a range of algal species and culturing conditions. However, more often than not, the analyses are incomplete

and are not reported on a consistent basis (*e.g.* as-received, air-dried, dry and ash-free). This makes direct comparison between different types of algae difficult. A survey of the peer-reviewed literature has been carried out in order to compare the fuel properties of micro- and macroalgal biomass to that of coal and commonly used terrestrial biomass fuels. The survey encompasses a broad range of both freshwater and marine species of micro- and macroalgae. Proximate, ultimate, and heating value analyses are presented in Table 1 and elemental analyses of the main inorganic elements in Table 2. Mean and range values are presented for different categories of algal biomass (freshwater microalgae, marine microalgae, freshwater macroalgae, and marine macroalgae), for coal, and for commonly used terrestrial biomass fuels. All results have been converted to consistent bases to enable direct comparison between the different fuel categories.

Table 1. Survey of proximate, ultimate, and heating value analyses reported in the literature for different types of algal biomass, coal, and terrestrial biomass fuels. Range values are shown below the mean value. The number of samples included in the survey is indicated in parentheses.

	algal biomass					terrestrial biomass [16-19]				coal[a] [19, 20]
	microalgae		macroalgae		references	wood and wood-derived	straws	grasses	other agricultural	
	freshwater	marine	freshwater	marine						
proximate analysis										
volatile matter (%, daf[b])	76.3 61.7 - 87.4, (6)	79.8 63.0 - 89.2, (4)	85.4 77.3 - 98.4, (7)	70.3 55.5 - 84.3, (16)	[15, 21-35]	80.9 72.5 - 87.4, (28)	81.2 78.1 - 85.5, (9)	83.0 80.6 - 85.6, (10)	77.8 61.0 - 87.3, (24)	42.0 14.8 - 60.5, (37)
fixed carbon (%, daf)	23.7 12.6 - 38.3, (6)	20.2 10.8 - 37.0, (4)	14.6 1.6 - 22.7, (7)	29.7 15.7 - 44.5, (16)	[15, 21-30, 32-35]	19.1 12.6 - 27.5, (28)	18.8 14.5 - 21.9, (9)	17.0 14.4 - 19.4, (10)	22.2 12.7 - 39.0, (24)	58.0 39.5 - 85.2, (37)
ash (%, db[c])	12.6 1.0 - 37.8, (17)	23.8 6.4 - 62.8, (38)	14.7 2.9 - 35.8, (15)	23.7 9.0 - 59.0, (31)	[15, 21-46]	3.5 0.1 - 16.5, (28)	8.6 4.7 - 20.1, (9)	4.3 0.8 - 9.4, (10)	5.0 1.4 - 18.0, (24)	20.9 5.7 - 52.0, (37)
ultimate analysis										
C (%, daf)	51.1 40.7 - 61.3, (10)	50.8 43.7 - 57.8, (13)	48.5 46.7 - 50.6, (10)	45.5 37.1 - 52.9, (12)	[15, 22, 23, 28-32, 34, 36-38, 40, 41, 43]	52.1 48.7 - 57.0, (28)	49.4 48.5 - 50.6, (9)	49.2 46.1 - 52.0, (10)	50.2 42.2 - 58.4, (24)	78.2 62.9 - 86.9, (37)
H (%, daf)	7.5 6.5 - 9.1, (10)	6.9 5.0 - 8.0, (13)	7.0 6.3 - 7.5, (10)	6.5 5.6 - 7.5, (10)	[15, 22, 23, 28-32, 34, 36-38, 40, 41, 43]	6.2 5.4 - 10.2, (28)	6.1 5.6 - 6.4, (9)	6.1 5.1 - 6.5, (10)	6.3 3.2 - 9.2, (24)	5.2 3.5 - 6.3, (37)
N (%, daf)	7.7 2.1 - 10.0, (16)	7.3 2.3 - 11.6, (20)	4.4 2.0 - 5.4, (10)	3.4 1.2 - 6.9, (12)	[15, 22, 23, 28-32, 34, 36-41, 43, 45]	0.4 0.1 - 0.7, (28)	1.2 0.5 - 2.8, (9)	0.9 0.3 - 2.6, (10)	1.4 0.1 - 3.4, (24)	1.3 0.5 - 2.9, (37)
O (%, daf)	33.0 27.0 - 46.3, (10)	34.7 25.7 - 49.0, (3)	39.2 37.0 - 42.7, (10)	42.1 30.5 - 49.2, (12)	[15, 22, 23, 28-30, 32, 34, 36-38, 40, 41]	41.2 32.0 - 45.3, (28)	43.2 40.1 - 44.6, (9)	43.7 42.5 - 44.5, (10)	41.9 34.2 - 49.0, (24)	13.6 4.4 - 29.9, (37)
S (%, daf)	0.79 0.10 - 1.7, (15)	1.5 0.10 - 2.5, (9)	0.28 <0.01 - 1.6, (10)	2.7 0.99 - 8.9, (12)	[15, 22, 28-32, 34, 36, 37, 39, 40, 44, 45, 47-49]	0.08 0.01 - 0.42, (28)	0.15 0.08 - 0.28, (9)	0.13 0.04 - 0.27, (10)	0.16 0.01 - 0.60, (24)	1.7 0.2 - 9.8, (37)
HHV (MJ kg^{-1}, daf)	24.9 22.5 - 29.7, (10)	23.4 16.5 - 28.7, (8)	19.9 16.7 - 22.2, (14)	20.0 15.4 - 23.2, (17)	[28-32, 35, 36, 40-42, 45, 46]	21.7 18.7 - 28.0, (30)	19.8 19.6 - 20.0, (4)	19.4 19.0 - 19.8, (8)	22.3 20.2 - 24.4, (7)	33.3 30.1 - 34.7, (11)

[a]Coals sourced from a wide range of geographical locations (9 countries) and include lignite, sub-bituminous, and bituminous ranks. [b]daf = dry and ash-free basis. [c]db = dry basis

Table 2. Concentrations of the main inorganic elements in different types of algal biomass, coal, and terrestrial biomass fuels. Range values are shown below the mean value. The number of samples included in the survey is indicated in parentheses.

	algal biomass					terrestrial biomass [16, 18, 19, 50-57]				coal [19, 58]
g kg^{-1}	microalgae		macroalgae		references	wood and wood-derived	straws	grasses	other agricultural residues	
dry basis	freshwater	marine	freshwater	marine						
Cl	4.0 <0.1 - 16, (5)	36 0.5 - 77, (6)	3.9 3.6 - 4.1, (2)	31 15 - 52, (4)	[29, 31, 32, 34, 36, 59, 60]	0.20 0.1 - 0.50, (28)	4.1 0.30 - 6.4, (9)	2.1 0.40 - 8.3, (10)	0.90 0.10 - 2.1, (24)	0.30 0.10 - 1.1, (34)
P	12 0.04 - 46, (9)	15 4.0 - 33, (16)	6.9 4.8 - 9.6, (5)	12 0.77 - 29, (10)	[15, 31, 32, 34, 36, 38, 43, 47, 48, 60-62]	1.2 <0.01 - 5.1, (21)	0.71 0.17 - 1.2, (7)	2.8 0.40 - 7.6, (18)	1.6 0.04 - 12, (11)	0.36 0.06 - 0.92, (14)
K	10 0.50 - 24, (10)	11 4.0 - 19, (11)	22 13 - 31, (5)	34 7.3 - 78, (10)	[15, 31, 32, 34, 36, 38, 44, 45, 48, 59-63]	4.6 0.22 - 24, (22)	10 2.8 - 15, (7)	11 1.0 - 36, (18)	7.8 0.97 - 25, (11)	1.9 0.50 - 3.9, (14)
Na	7.0 0.08 - 27 (8)	50 6.6 - 240, (11)	7.3 0.95 - 14, (4)	39 14 - 77, (10)	[15, 31, 32, 34, 36, 38, 44, 45, 59-63]	0.03 <0.01 - 0.18, (22)	0.13 0.05 - 0.27, (7)	0.31 0.06 - 0.80, (4)	0.51 0.01 - 4.7, (11)	1.1 0.15 - 3.1, (14)
Ca	6.6 <0.01 - 41, (10)	16 0.90 - 35, (10)	3.7 2.7 - 4.8, (5)	18 10 - 35, (10)	[15, 31, 32, 34, 38, 44, 45, 47, 48, 59-63]	5.3 0.64 - 16, (22)	4.4 2.8 - 8.3, (7)	4.3 3.1 - 7.0, (18)	3.6 0.56 - 7.4, (11)	4.4 0.15 - 9.2, (14)
Mg	6.7 0.24 - 22, (10)	9.5 0.67 - 50, (11)	3.4 2.4 - 45, (5)	8.4 4.3 - 12, (10)	[15, 31, 32, 34, 36, 38, 44, 45, 48, 59-63]	0.77 0.09 - 2.9, (22)	0.82 0.27 - 1.8, (7)	2.6 0.83 - 4.8, (13)	1.3 0.20 - 4.5, (11)	1.7 0.45 - 4.8, (14)
Si	37 11 - 63, (2)	29 0.50 - 220, (10)	1.2 1.0 - 1.3, (2)	3.1 0.58 - 7.1, (9)	[15, 31, 32, 34, 43]	0.65 0.03 - 6.6, (22)	13 0.35 - 20, (7)	8.8 6.0 - 9.9, (6)	23 0.26 - 87, (11)	28 8.5 - 54, (14)
Fe	10.7 0.05 - 36, (9)	1.5 <0.01 - 3.6, (9)	2.1 1.1 - 4.9, (5)	2.1 0.04 - 3.8, (9)	[15, 31, 32, 34, 36, 44, 45, 47, 59, 60, 62]	0.05 <0.01 - 0.17, (18)	0.29 0.03 - 0.74, (7)	0.17 0.04 - 0.42, (20)	0.30 0.05 - 0.91, (11)	5.9 1.4 - 10, (14)
Al	0.10 (1)	nd[a]	0.06 0.02 - 0.16, (4)	2.1 0.03 - 6.4, (9)	[15, 31, 32, 34, 62]	0.16 <0.01 - 0.91, (22)	0.40 0.07 - 1.1, (7)	0.12 0.02 - 0.55, (9)	0.33 0.04 - 1.2, (11)	15 5.8 - 24, (14)

[a]nd = no data

The proximate analyses (Table 1) show a large range of ash contents for both microalgae (1.0 – 62.8% w/w) and macroalgae (2.9 – 59.0% w/w). Ash content is generally greater for marine algae than for freshwater algae and is on average greater for algal biomass than for terrestrial biomass. The relative proportions of fixed carbon and volatile matter in algal biomass more closely resemble the proportions in terrestrial biomass than in coal. Coal generally contains much higher levels of fixed carbon and lower levels of volatile matter than biomass.

The ultimate analyses (Table 1) show only minor differences between the concentrations of C and H in algal biomass and the concentrations of these elements in terrestrial biomass, on a dry and ash-free basis. Coal, on the other hand, contains more C and less H than algae. Mean O concentrations for macroalgae are generally similar to that of terrestrial biomass and are slightly higher than that of microalgae. Nitrogen concentrations are generally much higher in algal biomass than in terrestrial biomass and coal. This has been attributed to high protein contents in algae [15, 64], and to the ability of many algae to store excess N to that needed for immediate growth [65]. Sulphur contents vary widely in both micro- and macroalgae and can significantly exceed values reported in terrestrial biomass. Marine algae generally contain more S than freshwater algae, which could be expected given that seawater contains higher concentrations of sulphate ions than does freshwater [66].

Higher heating values (HHVs) reported for microalgae are on average higher than that reported for macroalgae and terrestrial biomass when compared on a dry and ash-free basis (see Table 1). This is likely due to lower O contents in microalgae. Mean HHVs for freshwater and marine macroalgae lie within the range commonly reported for terrestrial biomass.

The major and minor inorganic elements in micro- and macroalgae (Table 2) generally include Cl, P, K, Na, Ca, Mg, Si, and Fe. A wide range of concentrations has been reported in the literature for these elements. Reported values can vary by as much as two orders of magnitude. Nevertheless, some general trends are evident between the different categories of algae. Silicon levels tend to be much higher in microalgae than in macroalgae. Concentrations of Cl, Na, and Ca are generally greater in marine algae than in freshwater algae which reflects the differences in the concentrations of these elements in fresh and marine waters [66]. When compared with terrestrial biomass,

algae generally contain higher concentrations of the alkali metals (K and Na) and the alkaline earth metals (Ca and Mg). On average, freshwater algae have similar Cl contents to straw. Chlorine levels in marine algae tend to be much higher. The concentration of P is generally greater in algal biomass than in coal and terrestrial biomass. Furthermore, the concentration of P in algae often exceeds that of Si, particularly in macroalgae.

Studies which report the concentrations of the trace elements (TEs) in algal biomass are limited. Most studies report only the concentrations of a select few TEs which are of relevance to that particular study. Nevertheless, the available studies show that many species of algae are capable of sequestering large quantities of TEs from their growth media. TE concentrations reported in the literature are presented in Table 3 for a range of cultivation environments including both freshwater and seawater as well as two types of industrial wastewater. Table 3 indicates that algae which have been cultivated in seawater may contain elevated levels of As, B, Pb, Se, and Zn. A species of microalgae (*Spirulina* sp.), which had been cultivated in effluent from a copper smelter and refinery in Poland, was found to contain high concentrations of Cu, Cd, Hg, and Ni [67]. Macroalgae (*Hydrodictyon* sp., *Oedogonium* sp., and *Rhizoclonium* sp.), which had been cultivated in ash-dam water (ADW) from a coal-fired power station in North-East Australia, were found to contain elevated concentrations of As, B, Se, V, and Zn [62].

Table 3. Trace element concentrations in algal biomass which have been cultivated in different growth media

Element (ppm, db[a])	Growth medium			
	seawater [68, 69]	freshwater + f2 media[b] [62]	ash-dam water + f2 media [62]	copper smelter and refinery effluent [67]
Ag	<1			
As	63 - 94	<1 - 2	81 - 137	
B	125 - 222	4 - 14	247 - 533	
Ba	13 - 120			53
Cd	2	<1	<1	463
Co	<1 - 2			12
Cr	<1 - 9	<1 - 2	4 - 6	
Cu	3 - 210	9 - 13	42 - 85	271
Hf				3
Hg		<1	<1	1340
Li	2 - 8			
Mn	9 - 800	104 - 697	986 - 1500	263
Mo	<1 - 1	<1 - 7	3 - 26	
Ni	2 - 74	<1	3 - 4	194
Pb	2 - 26	<1 - 2	1	4
Rb	80 - 250			
Re				42
Sb				3
Se	8 - 14	<1	11 - 22	
Sn	<1 - 3			
Sr	420 - 2800	27 - 70	402 - 681	
Th				33
Ti	2 - 308			
V	<1 - 12	<1 - 3	832 - 1543	
Zn	40 - 884	29 - 36	699 - 1437	166

[a]db = dry basis. [b]f2 media = a standard nutrient medium containing nitrate, phosphate, and trace amounts of the following metals: Co, Cu, Fe, Mn, Mo, Na, and Zn.

2.3.1. Implications for thermochemical processing

Both micro- and macroalgal biomass tend to contain high concentrations of various inorganic impurities. Many of these impurities are intimately connected with major operational problems in the main technologies used to thermally process biomass fuels, namely fluidised-bed (FB), fixed-bed, and entrained-flow reactors. Accurate prediction and effective mitigation of these operational problems requires prior knowledge of the behaviour of these inorganic impurities during thermochemical conversion.

Operational problems associated with inorganic impurities in the fuel can often be alleviated by operating at lower temperatures. However, low operating temperatures

may compromise burnout of the organic fraction of the fuel which can lead to increased emissions of pollutants such as CO, soot, and polyaromatic hydrocarbons (PAHs) [10]. Consequently, the choice of operating temperature in practical thermochemical processes often involves a trade-off between maximising the extent of fuel conversion and mitigating operational problems. The extent of fuel conversion during pyrolysis, combustion, or gasification of algal biomass will not only depend on the operating conditions but also on the inherent reactivity of algae as a fuel.

The high concentrations of N in algal biomass indicate significant potential for the formation of NO_x during combustion. The term "NO_x" refers collectively to the following oxides of nitrogen: NO and NO_2. These two species are harmful atmospheric pollutants. Both are acid rain precursors and participate in the formation of photochemical smog [70]. NO_x is mainly emitted in the form of NO during the combustion of coal and biomass [70]. There are three established pathways for the formation of NO during combustion [71]: oxidation of atmospheric N_2 (thermal-NO); reactions between fuel-derived radicals with atmospheric N_2 (prompt-NO); and oxidation of N chemically bound to the fuel (fuel-NO). Of these pathways, fuel-NO is generally dominant at the low combustion temperatures used to process biomass fuels [70]. The emission of NO_x during the combustion of algal biomass will therefore largely depend on the conversion of fuel-N to NO.

The use of algal biomass for the treatment of wastewater has long been promoted [72]. Algae are renowned for their abilities to remove inorganic N and P, break down organic toxins (*e.g.* hydrocarbons, biocides, and surfactants), and sequester potentially toxic trace metals and metalloids from municipal, agricultural, and industrial wastewaters [8, 73]. The utilisation of algal biomass which has been produced for the bioremediation of ADW from coal-fired power stations has gained recent commercial interest [74-76]. The produced biomass has several advantages as a feedstock for heat and power applications. Much of the infrastructure required for thermochemical processing is likely already available at the power station and the volume of bio-solids is substantially reduced in the process, which is beneficial from the point of waste management. However, previous studies [62, 74] have shown ADW algae to contain high concentrations of potentially toxic TEs. If released into the environment, these elements may cause harm to delicate ecosystems and to human health. The potential for

TE mobilisation must therefore be considered before ADW algae can be safely used as a feedstock in thermochemical processes.

2.4. Oxidation of carbon and char reactivity

Several experiments [15, 27, 64] have been carried out in order to compare the decomposition of algal biomass in thermochemical processes with that of terrestrial plants. These experiments all involved heating small samples of biomass (<50 mg) in a thermobalance at a controlled rate and simultaneously monitoring sample weight loss and differential temperature or heat flow as a function of time and furnace temperature. When compared with wood, the onset of volatile release and the maximum rate of weight loss generally occur at lower temperatures for micro- and macroalgae, which indicates relatively high reactivities for algal biomass in thermochemical processes. Various authors [15, 27, 64, 77] have attributed these trends to differences in the main organic constituents in algal biomass and wood. The main constituents of wood are lignin, cellulose, and hemicellulose [78]. Algae generally contain much higher contents of protein, lipid, and simple carbohydrates [15, 64, 77]. These components decompose more readily upon heating than lignin, cellulose, and hemicellulose [27, 64, 77]. However, the low heating rates (<2 °C s^{-1}) used in the aforementioned thermobalance experiments poorly simulate conditions inside industrial reactors, where the heating of fuel particles is typically rapid (100 – 2000 °C s^{-1}). Numerous studies [79-81] have shown the fuel heating rate to have a significant impact on fuel particle transformations in thermochemical processes. Consequently, the decomposition of algal biomass in industrial reactors may differ substantially from that encountered in the thermobalance experiments reported by previous investigators.

When a solid fuel particle is first introduced into an industrial combustor the particle dries and devolatilises, forming a residual char. Oxidation of the evolved volatiles is rapid, and generally follows as quickly as the volatiles are released from the fuel. The residual char is oxidised, through heterogeneous reactions between the solid char residue and atmospheric oxygen. Devolatilisation is a much faster process than char oxidation, and therefore, the rate of combustion in industrial installations largely depends on the partitioning between volatiles and char. Experience burning both coal [82] and terrestrial biomass [83] has shown the partitioning between volatiles and char to depend not only on operating conditions (*e.g.* temperature and gas atmosphere) but also on the type of fuel. One way of determining the partitioning between volatiles and

char is to track the conversion of C throughout the entire combustion process. This can be done by monitoring the concentrations of the products of C combustion (primarily CO and CO_2) in flue gas emissions released during the combustion of a small sample of fuel. The release of C during the combustion of algal biomass has so far only been monitored at low-heating rates (<2 °C s^{-1}) [30, 64, 84]. In order to partition the release of C between volatiles and char under conditions relevant to industrial combustion processes, the release of C should be tracked at higher fuel heating rates.

Char conversion is the slowest step in industrial combustion and gasification processes, and therefore, generally determines the total conversion of carbon. For this reason there have been numerous studies on the reactivity of coal [85-87] and terrestrial biomass [88-91] chars. These studies have shown char reactivity to depend on the physical and chemical properties of the char which in turn depend on the inherent properties of the fuel [92] as well as on the devolatilisation conditions [79]. Certain inorganic elements are known to have a significant impact on char reactivity. There is strong consensus in the literature that the alkali metals, K and Na, catalyse char reactivity. The alkaline earth metals, Ca and Mg, are understood to catalyse char reactivity, but to a lesser extent than the alkali metals [89, 91]. Silicon has been reported to reduce char reactivity by forming inactive alkali silicates [89]. The overall catalytic effect of the inorganic matter likely depends on the relative proportions of the inorganic elements in the char.

The concentrations of the inorganic elements in algal biomass differ substantially from that in both coal and terrestrial biomass fuels. Despite this, limited work has been done to characterise the reactivity of algal chars under conditions relevant to industrial combustion and gasification processes. Kirtania *et al.* [23, 93] studied the gasification reactivity of microalgal chars prepared at both low and high heating rates. The heating rate was found to have little influence on the structure and reactivity of the char [23]. Direct comparisons between wood and microalgal chars [93] indicate slightly higher gasification reactivities for wood under most conditions. Other than the recent work by Kirtania *et al.* [23, 93], little has been done to assess the reactivity of microalgal chars. There are no known studies on the reactivity of macroalgal chars.

2.5. Conversion of fuel-N to NO

There have been numerous studies on the conversion of fuel-N during the combustion of coal and terrestrial biomass fuels, *e.g.* [70, 71, 94, 95]. These studies show the extent

of fuel-N conversion to NO to depend not only on the combustion environment (*e.g.* temperature and stoichiometry) but also on the physical and chemical properties of the fuel. Comparisons between different types of terrestrial biomass fuels indicate that the fuel-N content has a significant influence on the formation of NO. Various authors [83, 96, 97] have reported a trend of diminishing fuel-N conversion to NO with increasing fuel-N content during the combustion of terrestrial biomass fuels. Winter *et al.* [96] and Giuntoli *et al.* [83] attributed this trend to differences in the extent of reduction of NO to N_2 by gas phase species, HCN and NH_3. According to these authors, these two species and their related radicals are formed in greater quantities, and are consequently present in the gas phase in higher concentrations during the combustion of N-rich fuels. The potential for NO reduction to N_2 is therefore greater, and the resultant conversion of fuel-N to NO lower, for N-rich biomass. The trend of diminishing conversion of fuel-N to NO with increasing fuel-N content is less clear in the case of coal [97].

Experience burning coal and terrestrial biomass fuels has shown the mechanisms for NO formation to differ depending on whether fuel-N is released during devolatilisation or char oxidation [94]. The effective control of NO_x in industrial combustors therefore not only requires knowledge of the total conversion of fuel-N to NO, but also knowledge of the partitioning between volatile-N and char-N. Stoichiometric measures, based on delayed fuel-air mixing to promote NO reduction to N_2, are commonly employed to minimise the amount of NO formed from volatile-N [94]. The control of NO formed from char-N is more difficult [98], and is a subject of ongoing research [99].

There are only a few studies which address the thermal behaviour of N in algal biomass, and most of these studies have focused on conditions relevant to pyrolysis processes. Emissions of HCN, CH_4N, and C_3H_8N have been detected [34, 84], in descending order of concentration, during the slow pyrolysis (<2 °C s^{-1}) of microalgae. Ross *et al.* [69] analysed emissions of nitrogenous species during the fast pyrolysis (500 °C) of three samples of marine macroalgae, using pyrolysis-gas chromatography mass-spectrometry (py-GC/MS). They inferred that the released N mainly originated from aromatic compounds, particularly analogues of indole and pyrrole. Trinh *et al.* [77] measured the concentration of N in the char residue produced during the fast pyrolysis (550 °C) of *Ulva lactuca*, a marine species of macroalgae. The concentration of N in the char was

greater than that in the alga itself, which indicates significant retention of N during pyrolysis at low temperatures.

Wang *et al.* [30] monitored emissions of NO and NO_2 during the fixed-bed combustion of two species of marine macroalgae. They reported the onset of NO release to commence at around 200 – 300 °C and the cumulative release of NO to be much greater than that of NO_2, which is consistent with the combustion behaviour of N in terrestrial biomass fuels [70, 100]. However, the combustion experiments performed by Wang *et al.* [30] were all carried out at low heating rates (<2 °C s^{-1}) and the gas phase measurements of NO and NO_2 were not quantitative. Consequently, the experiments did not show the total conversion of fuel-N to NO or the partitioning of the released NO between volatile-N and char-N. This information is needed for the development of effective control strategies to minimise NO_x emissions during the combustion of algal biomass in industrial-scale reactors.

2.6. Inorganic matter and ash-related issues

The inorganic matter in biomass is responsible for major operational problems in industrial thermochemical reactors. Fouling, ash deposition, high-temperature corrosion, and bed agglomeration are all caused by transformations of the inorganic matter during thermal conversion [11, 12, 101], and are collectively referred to in the literature as ash-related issues. The first three issues are relevant to fluidised-bed (FB), fixed-bed, and entrained-flow reactors whereas bed agglomeration is specifically relevant to FB reactors. The consequences of ash-related issues can be severe. Plugging of boiler tube channels [102], erosion of gas turbine components [103], and bed defluidisation [104] have all been reported. The fate of the inorganic matter during thermal conversion and its role in ash-related issues not only depend on the concentrations of the major and minor inorganic elements in the fuel but also on their speciation or occurrence modes in the fuel.

2.6.1. Speciation of the inorganic matter

The speciation of the inorganic matter has been studied extensively in both coal [20, 105] and terrestrial biomass fuels [19, 106]. In these fuels, the inorganic matter is commonly categorised into the following forms: ionic salts; inorganic matter which is organically bound to the carbonaceous matrix; and included and excluded minerals. Included minerals refer to minerals which are precipitated inside the fuel as part of

natural processes and excluded minerals refer to minerals which have been added to the fuel during fuel processing steps. The inorganic matter in coal predominately consists of minerals. Biomass on the other hand, tends to contain much higher proportions of ionic salts and organically associated inorganic matter. These forms are generally more mobile during thermochemical conversion than mineral matter, and consequently, have a higher tendency to participate in ash-related issues [107].

Comparatively little work has been done to determine the speciation of the inorganic matter in algal biomass. Most studies in this field have focused on the occurrence of P in microalgae, since P is one of the most important growth limiting factors in microalgal biotechnology [108]. Several species of microalgae are known to be capable of storing large amounts of P, in excess to that required for essential metabolic processes (*e.g.* nucleic acid synthesis), in the form of inorganic polyphosphates (polymers consisting of orthophosphate units linked together by phosphoanhydride bonds) [109, 110]. It is understood that P contained in inorganic polyphosphates is converted to organic forms when the availability of P becomes limited [111]. Like P, S is also known to occur in microalgae in both organic and inorganic forms [111].

The association of Si has mainly been studied in diatoms. In diatoms, Si occurs primarily as amorphous silica, within cell walls [112]. Ross *et al.* [69] studied the leaching behaviour of the alkali metals (K and Na) and the alkaline earth metals (Ca and Mg) in three samples of marine macroalgae which had been rinsed in freshwater after harvesting. Approximately 30 - 40% of the total K, Na, and Mg were water extractable. Calcium was virtually insoluble in water however was highly soluble (>90%) in a 2M solution of HCl. It is likely that the water extractable fractions of K, Na, Ca, and Mg would have been higher had the samples not been previously rinsed in freshwater. Ross *et al.* [69] proposed that the alkali and alkaline earth metals in brown macroalgae are largely associated with alginate, the salt of alginic acid, based on the leaching behaviour of these elements and on GC/MS analyses of product gases released during low-temperature (500 °C) pyrolysis of the macroalgal samples. Borowitzka *et al.* [113] examined Ca-containing mineral deposits in a diverse range of algae using microscopic methods and concluded that calcite and aragonite were the main mineral forms of Ca in both freshwater and marine algae.

The limited literature available on the speciation of the inorganic elements in algal biomass tends to focus on individual elements in isolation of the other main inorganic elements. Furthermore, most of the literature in this field is non-quantitative and encompasses only a narrow range of algal species. More quantitative analysis is needed in order to develop a comprehensive understanding of the occurrence modes of the main inorganic elements in algal biomass.

2.6.2. Fluidised-bed technologies and bed agglomeration

Fluidised-bed (FB) technologies offer good fuel flexibility *i.e.* they are capable of handling a wide range of fuels which vary in size, shape, and chemical composition [114]. For this reason they are often favoured for the conversion of biomass fuels. In FB reactors a bed of inert particles is contacted with an upwards flowing gas so that the inert particles attain a liquid-like state. The inert bed particles are used to promote stable fluidisation of the incoming fuel particles and to enhance heat transfer. During combustion or gasification, various inorganic components in the fuel are retained in the bed as ash. The ash may interact with the inert bed particles in such a way that causes the bed particles to agglomerate [12]. Bed particle agglomeration disrupts stable fluidisation by increasing resistance to the upwards flowing gas, and may eventually lead to the bed defluidising [104].

Most of the previous research on bed agglomeration has focused on coal and terrestrial biomass fuels. Skrifvars *et al.* [115] established three major mechanisms for the sintering of coal ashes: partial melting; viscous-flow sintering; and gas-solid chemical reaction. Viscous-flow sintering tends to be the dominant mechanism for anthracite and bituminous coals [115] whereas partial melting tends to be the dominant mechanism for brown coals [115], because brown coal contains a higher proportion of low-temperature melting matter in its ashes. Partial melting can lead to the formation of a sticky ash coating on the outside of burning char particles, which in a FB environment, can transfer to bed particles and act as glue for agglomerate formation [116]. This process is known as melt-induced agglomeration and can occur during the conversion of both coal and terrestrial biomass fuels [117]. Bed agglomeration can also be initiated by chemical reactions between the bed particles and gas or liquid phase alkali species originating from the fuel. This process is known as coating-induced agglomeration and is the principal mechanism of bed agglomeration for many terrestrial biomass fuels [118]. The principal mechanism of bed agglomeration can differ from fuel to fuel and appears to

depend largely on the composition of the inorganic matter in the fuel. The inorganic matter in algal biomass is distinctively different from that in both coal and terrestrial biomass. This makes it difficult to predict bed agglomeration during the conversion of algal biomass based solely on experience with coal and terrestrial biomass fuels.

Previous research into the FB conversion of algal biomass is limited to only a few recent studies [32, 119, 120], which have predominately focused on gasification conditions. Alghurabie *et al.* [119] attempted to gasify *Tetraselmis* sp., a marine species of microalgae, in a spouted FB reactor, however, were unable to achieve steady operation, due partly to attrition of microalgae in the fuel feeding system. Yang *et al.* [120] reported bed agglomeration during the co-gasification of wood and *Spirulina* sp., a species of microalgae, in a bubbling FB reactor, however, did not investigate the cause of agglomeration. Zhu *et al.* [32] conducted co-gasification trials in a similar reactor setup to that used by Alghurabie *et al.* [119], using a range of fuel mixtures containing 10% w/w algae and the balance brown coal. Two species of macroalgae and a species of microalgae were used in the fuel mixtures. In most trials, the authors reported severe bed agglomeration after only a few hours of operation. Based on analyses of bed material removed both during and post gasification, the authors attributed bed agglomeration to the formation of liquid alkali silicates on bed particles, in the case of the macroalgae/coal mixtures, and to the formation of an Fe-Al silicate eutectic mixture, in the case of the microalgae/coal mixture. Although the coal sample contained significantly less ash than the algal samples, it is still likely that the coal ash played a significant role in the bed agglomeration processes reported by Zhu *et al.* [32]. There are no known studies on the interactions that take place between pure algal ashes and bed material under conditions relevant to FB reactors.

2.6.3. Release of Cl, S, P, K, and Na

The release of volatile inorganic elements, particularly Cl, S, P, K, and Na, to the gas phase is intimately connected with fouling, ash deposition, and high-temperature corrosion in industrial pyrolysis, combustion, and gasification processes. Sulphur and Cl tend to be highly volatile during thermal conversion [55, 121]. Volatilised S compounds can condense on reactor surfaces (*e.g.* superheater tubes) to form hard deposits [122]. The release of Cl accelerates high-temperature corrosion [101] and often facilitates the release of the alkali metals, K and Na [11, 97]. The alkali metals are well known for forming low-temperature melting compounds which cause the formed ash to

become sticky. Their release leads to the deposition of ash particles both inside and downstream of the reactor [97, 122]. Phosphorous generally has a higher affinity for the alkali metals than its main competitors, Cl, S, and Si [123]. This property makes the release of P pivotal to the behaviour of the alkali metals. Phosphorous can react with the alkali metals to form molten alkali phosphates (*e.g.* KPO_3) [124] which volatilise at low temperatures [125] and contribute to fouling and ash deposition [126]. However, P can also react with the alkali metals to form stable, high-temperature melting, alkaline earth metal-rich, alkali phosphates (*e.g.* $CaK_2P_2O_7$) [124, 127] which remain in the char or ash, and thereby prevent the release of the alkali metals.

The precise role of Cl, S, P, K, and Na in ash-related issues largely depends on the extent to which these elements are released to the gas phase or are retained in the ash (or char) residues during fuel particle burnout. For this reason, a vast amount of research has been dedicated to understanding the volatile behaviour of these elements.

There is consensus in the literature [55, 121, 128] on the mechanisms governing the release of Cl. Chlorine is generally released by two main mechanisms when present in the fuel in the form of inorganic metal chlorides (*e.g.* KCl and NaCl). Mechanism (1) involves incorporation of the metal cation into proton donor sites in the char matrix (*e.g.* carboxyl groups) [128, 129] and the simultaneous release of Cl to the gas phase as HCl vapour. The release of HCl has been shown to commence at around 200 - 300 °C during the pyrolysis of both coal [130] and terrestrial biomass [131]. Mechanism (2) involves direct sublimation of metal chlorides, particularly KCl and NaCl, and is thought to only become significant at temperatures above 700 °C [121]. The principal mechanism of release appears to depend on the absolute content of Cl in the fuel. For Cl-lean fuels (<0.6% w/w), Mechanism (1) tends to dominate. For Cl-rich fuels (>0.6% w/w), Mechanism (2) tends to dominate, since release by Mechanism (1) is limited by the availability of proton donor sites in the char matrix for alkali capture.

Numerous studies [132-135] have shown the release of S to take place via two steps during the combustion and gasification of terrestrial biomass fuels. Step (1) occurs at low temperatures (<500 °C) during pyrolysis, and Step (2) at higher temperatures, during combustion or gasification of the residual char. It is understood that S which is organically bound to the fuel matrix is released during Step (1), as a result of destruction of the organic matrix [132, 133], and that inorganic forms of S are released

later, during Step (2) [132, 133, 135]. The amount of S released in each step has been found to correlate with the distribution of S between organic and inorganic forms in the fuel [133]. Mechanisms proposed for the release of inorganic S include vaporisation of alkali sulphates [121] and metal sulphate decomposition [121, 133], involving incorporation of the metal cation into the ash residue and the release of SO_2 (combustion) [132, 136] or H_2S and COS (gasification) [54, 137] to the gas phase. A number of studies [55, 128, 133] have indicated that the primary release of S is significantly affected by the availability of base cations in the char, particularly Ca. Secondary capture of gaseous SO_2 by organic functional groups in the char matrix is known to significantly reduce the net release of S from combustion processes [138, 139].

Studies which address the release of P are limited, since the concentration of P in coal and most commonly used terrestrial biomass fuels is generally low. Wu *et al.* [125] measured the release of P and K from bran during pyrolysis and combustion in a laboratory-scale, fixed-bed reactor. The majority (60 - 70%) of the total P was released by 1100 °C during combustion, whereas less than 10% of the total P was released during pyrolysis at the same temperature. The release of K was proportional to that of P under both pyrolysis and combustion conditions, within the temperature interval 700 – 1100 °C. Based on this result, Wu *et al.* [125] inferred that P is released by vaporisation of molten KPO_3. Bourgel *et al.* [140] modelled the release of P during the gasification of sewage sludge by means of thermodynamic equilibrium calculations. They predicted the release of P to commence at around 700 °C and that the extent of P release is greater for sewage sludge samples with higher P contents.

The volatile behaviour of the alkali metals, K and Na, is extremely complex and tends to vary substantially from fuel to fuel. Numerous mechanisms have been proposed in the literature for the release of the alkali metals and several authors have reviewed these for a diverse range of terrestrial fuels, including coal [141], agricultural crops [121, 128], wood, and wood-derived fuels [55]. Commonly reported mechanisms include: vaporisation of alkali salts (*e.g.* chlorides, sulphates, and phosphates); dissociation of alkali carbonates, alkali sulphates and alkali metals ion-exchanged to oxygen functionalities in the char matrix; and vaporisation of alkali silicates. In many cases, the alkali metals are released by a combination of these mechanisms. The importance of any given mechanism appears to depend largely on fuel composition. Certain

compositional parameters in particular, are known to play a key role in controlling the release of the alkali metals. Knudsen *et al.* [128] showed the release of K from agricultural crops to depend on the following molar ratios: K/Cl and K/Si. They proposed that K is preferentially released in the form of KCl until Cl becomes limiting and that the release of remaining K is inhibited by the formation of non-volatile silicates. The proposed retention of alkali metals in silicate compounds is consistent with experimental work by Kosminski *et al.* [142] and Steenari and Lindqvist [143], in which alkali silicates were identified in high-temperature ashes using X-ray diffraction (XRD) analysis.

The release of the inorganic elements from algal biomass has not been studied in nearly as much depth as has been done for coal and terrestrial biomass fuels. Several studies [30, 34, 64] have reported direct, gas-phase measurements for S. López-González *et al.* [34] showed the release of S to commence at around 200 – 300 °C during the temperature-programmed pyrolysis of three species of microalgae. Sulphur was predominately released below 600 °C, in the form of hydrogen sulphides, particularly H_2S, S_2H_2, and CH_3SH [34]. Wang *et al.* [30] monitored the release of SO_2 during the temperature-programmed combustion of two species of marine macroalgae. They reported two distinct peaks in the emission of SO_2, the first occurring between 200 and 400 °C and the second occurring between 500 and 700 °C. The dual peaks could imply that S is released by a two-step mechanism during combustion, which is consistent with the behaviour of S during the combustion of terrestrial biomass fuels. The gas-phase measurements made by López-González *et al.* [34] and Wang *et al.* [30] provide qualitative indications of the release of S during pyrolysis and combustion, however, the reported measurements are not fully quantitative, and therefore, do not show the extent to which S is released to the gas phase.

Quantitative studies on the release of the inorganic elements from algal biomass are scarce. Trinh *et al.* [77] determined the recovery of Cl, S, P, K, and Na in bio-oil and char residues following the fast pyrolysis (550 °C) of *Ulva lactuca*, a marine species of macroalgae. They reported high recoveries (>96%) for P, K, and Na. Recoveries for S and Cl were lower (91% and 65%), which indicates that these elements are partially released to the gas phase by 550 °C. Trinh *et al.* [77] reported similar recoveries for Cl, S, P, K, and Na during the pyrolysis of straw under the same experimental conditions. The release of the inorganic elements from algal biomass has not been quantified at

operating temperatures above 550 °C or in gas atmospheres relevant to combustion and gasification processes.

2.7. Mobilisation of trace elements

During fuel particle burnout the TEs are either released into the gas phase or are retained in the ash (or char) residues. Most volatilised TEs condense on fine particles in the product gases as the product gases are cooled, except for a few highly volatile TEs, such as Hg, Se, and B, which may partially remain in the gas phase [144]. The particles formed in the product gases typically follow a bimodal size distribution, with the first maximum occurring below 1 μm and the second maximum occurring above 1 μm [145]. Many toxic TEs preferentially condense on smaller particles in the product gases, and are often enriched in the submicron size fraction [146]. This makes their capture difficult, since conventional particulate control devices (*e.g.* electrostatic precipitators and bag filters) are generally least effective at removing particles within the size range 0.1 – 1 μm [146]. Consequently, volatilised TEs are often released from thermochemical processes in the form of submicron particles. Airborne particles below 1 μm in size readily penetrate into alveolar regions of human lungs, where the TEs can be taken up into the bloodstream [145]. Due to this, there are strict limits on the emissions of many TEs from industrial thermochemical processes [147]. This has motivated a vast amount of research into the volatility of the TEs during thermal conversion.

The volatility of the TEs has been studied in depth during the conversion of coal [148-150] and to a lesser extent during the conversion of terrestrial biomass [151-154]. Clarke and Sloss [144] developed a classification scheme which ranks the TEs in coal according to their relative volatility and expected fate during combustion. Their scheme provides a useful first-approximation of the volatility of the TEs during thermal conversion. However, the precise extent to which the TEs volatilise can vary substantially depending on the operating conditions and fuel composition.

Zevenhoven and Kilpinen [155] summarised the influence of key operational parameters on the volatility of the TEs. High operating temperatures and reducing gas atmospheres generally increase the extent to which many of the TEs volatilise. High operating pressures are understood to supress the volatility of the TEs but only to a relatively minor extent. The occurrence modes of the TEs and the presence of other

major and minor inorganic elements in the fuel are also known to influence TE volatility [148, 155]. High concentrations of Cl are known to promote the volatilisation of many TEs [154, 156]. Certain inorganic elements (*e.g.* Ca) have the opposite effect, and can help to retain various TEs in the fuel bed [149, 151].

Currently, there are no known studies which address the volatility of the TEs during the conversion of algal biomass in thermochemical processes. Moreover, it is difficult to predict the volatile behaviour of the TEs during the conversion of algal biomass based solely on knowledge gained from studies on conventional solid fuels, since the chemical composition of these fuels differs in many ways from that of algal biomass. Thus, the extent to which the TEs volatilise during the thermal conversion of algal biomass is largely unknown.

The consequences of TE mobilisation are compounded when utilising contaminated sources of biomass. When cultivated in ADW, algae are capable of sequestering high levels of various metals and metalloids [157], and as a result, often contain high concentrations of potentially toxic TEs when harvested [62]. The safe and effective use of ADW algae in thermochemical processes therefore requires assessment of the volatile behaviour of these TEs during conversion.

The TEs can undergo further fractionation post thermal conversion if the ash (or char) residues are contacted with water. TEs which have been leached out of ash or char can potentially migrate to and contaminate nearby waterbodies. Due to this, there have been numerous studies on the leaching behaviour of the TEs in char and ash residues produced during the conversion of coal and terrestrial biomass fuels. Several noteworthy reviews [158-160] have been published on this subject. In general, the extent of TE leaching from ash (or char) residues cannot be correlated with the leachable fraction in the fuel itself [161]. This result is not surprising given that the TEs undergo various physical and chemical transformations in thermochemical processes [158] which inevitably affect their resultant leaching behaviour. Under combustion conditions, the TEs tend to form oxides, hydroxides, and sulphates, whereas under gasification conditions, the formation of reduced species is more common [149]. Changes in the chemical speciation of the TEs may also be accompanied by changes in their spatial distribution [158]. Many TEs, particularly those which volatilise and recondense during thermal conversion (*e.g.* As, Sb, Se, and Zn), are known to become

enriched on char and ash particle surfaces where they are more susceptible to leaching [158].

The leachability of the TEs is also influenced by the behaviour of the major and minor inorganic elements during thermal conversion [159]. The formation of certain inorganic species in the ash (or char) residues can largely influence the pH of the leachate produced when the char or ash is first brought into contact with water [159]. The leachate pH is known to play a key role in controlling the extent of initial dissolution of the TEs as well as the precipitation of secondary phases, which collectively control the overall solubility of the TEs [158, 160].

Studies which address the leaching behaviour of the TEs in residues produced during the conversion of algal biomass in thermochemical processes are limited. Roberts *et al.* [74] investigated the leachability of several TEs in chars produced during the slow pyrolysis of a sample of macroalgae that had been cultivated in ADW at the Tarong Power Station in Queensland, Australia. The char samples generally contained higher total TE contents but lower water-extractable TE contents than the macroalga itself. In slightly more recent work, Roberts *et al.* [75, 76] measured the transfer of non-essential TEs from the produced chars to soil pore water and to plant biomass during the cultivation of a native grass and agricultural crops. There are no known studies on TE leaching from algal chars produced under fast pyrolysis conditions or from algal ashes produced under conditions relevant to combustion and gasification processes.

2.8. Limitations in the current literature

It is clear from the above review of literature, that several areas require significant improvement in order to develop a comprehensive understanding of the thermochemical fuel behaviour of micro- and macroalgal biomass.

Previous investigators have studied the decomposition of C and N during the combustion of algal biomass by burning small samples of algae (<50 mg) in a thermobalance and monitoring the emissions of gaseous products. However, the gas phase measurements of C and N in these experiments were not quantitative. Furthermore, the combustion experiments were all carried out at low heating rates, which poorly resemble conditions inside industrial reactors where heating of fuel particles is rapid. Thus, quantitative, time-resolved, gas-phase measurements of CO, CO_2, and NO during combustion at higher heating rates are recommended. Such

measurements will not only reveal the total conversion of C to CO and CO_2 and fuel-N to NO, but also the partitioning of the released species between volatiles and char.

Previous studies on the reactivity of algal chars have focused on a limited number of microalgal species, which have been cultivated under a narrow range of conditions. Consequently, it is largely unknown how char reactivity varies for different species of algae and for different cultivation environments.

A large range of both micro- and macroalgal species have been analysed for their elemental composition. The main inorganic elements generally include: Cl, S, P, K, Na, Ca, Mg, Fe, and Si. Currently, limited work has been done to determine the occurrence modes of these elements in algal biomass. The literature in this field is rarely quantitative and tends to focus on individual elements and on a narrow range of algal species. This has resulted in a knowledge gap which prevents accurate prediction of the role of the inorganic matter in ash-related issues.

There have been a few experimental studies on the thermal conversion of algal biomass in FB reactors. The authors of these studies reported difficulties in sustaining stable fluidisation and attributed these difficulties to bed agglomeration. Nevertheless, there has only been one formal investigation into bed agglomeration during the conversion of algal biomass. This study involved co-gasification trials with fuel mixtures containing only 10% w/w algae and the balance brown coal. There are no known studies where pure algal biomass has been used as the feedstock. Consequently, the precise interactions that take place between algal ashes and bed material under conditions relevant to FB processes remain unclear.

Experience from studies based on a vast range of coal and terrestrial biomass fuels, have shown the volatile behaviour of the inorganic elements to vary substantially depending on the chemical composition of the fuel. The chemical composition of algal biomass varies in many ways from that of coal and commonly used terrestrial biomass fuels, and can also vary significantly depending on the species of algae and cultivation environment. In spite of this, limited work has been done to characterise the release of volatile inorganic elements, particularly Cl, S, P, K, and Na, during the thermal conversion of algal biomass. Previous work in this field is mainly non-quantitative. The only known quantitative study has focused on just one species of algae and on a single set of operating conditions which are of relevance to low-temperature pyrolysis

processes. Hence, more extensive research is needed to characterise the release of the inorganic elements under a range of operating temperatures and gas atmospheres relevant to pyrolysis, combustion, and gasification processes.

Algal biomass which has been cultivated in ADW from a coal-fired power station has been found to contain high concentrations of various TEs. If released from thermochemical processes, these TEs may accumulate in the environment at harmful levels. The responsible use of ADW algae in thermochemical processes therefore requires prior knowledge of the fate of the TEs both during and post conversion. Currently, the only known studies on TE mobilisation during the utilisation of ADW algae have focused on the leaching behaviour of the TEs in char residues prepared under slow-pyrolysis conditions and on the subsequent transfer of the leached TEs to soil-pore water and to plant biomass. There are no known studies which address the volatility of the TEs or the leachability of the TEs in char and ash residues prepared in thermal processes relevant to heat and power applications, *i.e.* fast pyrolysis, combustion, and gasification.

2.9. Objectives of thesis

The aim of this thesis is to characterise the thermochemical fuel behaviour of micro- and macroalgal biomass. The detailed objectives are:

1. To compare the gasification reactivity of algal chars produced from different species of algae under pyrolysis conditions relevant to industrial gasification processes.
2. To characterise the conversion of fuel-C to CO and CO_2 and fuel-N to NO during combustion, and to partition the conversion of C and N between the different phases of fuel particle burnout.
3. To develop an improved understanding of the occurrence, particularly the speciation, of the main inorganic elements in algal biomass.
4. To gain new insights into the interactions that takes place between algal ashes and quartz bed material during FB combustion.
5. To determine the extent to which Cl, S, P, K, and Na are released in pyrolysis, combustion, and gasification processes and to explain the release of these elements in terms of mechanisms existing for coal and terrestrial biomass fuels.

6. To assess the mobility of 11 TEs (As, Be, Co, Cu, Mn, Ni, Pb, Sb, Se, V, Zn) during the thermal conversion of ADW algae, in terms of their tendency to volatilise and their potential to be leached from char and ash residues.

Chapter 3

Paper I

Combustion Behavior of Algal Biomass: Carbon Release, Nitrogen Release, and Char Reactivity

Daniel J. Lane[a], Peter J. Ashman[a], Maria Zevenhoven[b], Mikko Hupa[b], Philip J. van Eyk[a], Rocky de Nys[c], Oskar Karlström[b], and David M. Lewis[a]

[a]School of Chemical Engineering, The University of Adelaide, Adelaide, South Australia 5005, Australia

[b]Process Chemistry Centre, Åbo Akademi University, Piispankatu 8, Turku 20500, Finland

[c]School of Marine and Tropical Biology, James Cook University, Townsville, Queensland 4811, Australia

Energy & Fuels **2014**, 28 (1), pp. 41 – 51.

Statement of Authorship

Publication details: Lane DJ, Ashman PJ, Zevenhoven M, Hupa M, van Eyk PJ, de Nys R, Karlström O, Lewis DM. Combustion behavior of algal biomass: carbon release, nitrogen release, and char reactivity. Energy & Fuels 2014; 28 (1): 41-51.

Publication status: Published

Author contributions:

By signing the Statement of Authorship, each author certifies that their stated contribution to the publication is accurate and that permission is granted for the publication to be included in the candidate's thesis.

Daniel J. Lane (Candidate)
Under the supervision of P. J. Ashman, M. Zevenhoven, M. Hupa, and D. M. Lewis, I designed and performed the experiments, interpreted and processed the data, and wrote the manuscript.

Signed Date 16/10/2015

Peter J. Ashman
I supervised the candidate and evaluated the final version of the manuscript.

Signed Date 16/10/15

Maria Zevenhoven
I supervised the candidate, aided in the development of the experimental method, and evaluated the final version of the manuscript.

Signed Date 21/10/15

Mikko Hupa
I supervised the development of work, aided in the development of the experimental method, and evaluated the final version of the manuscript.

Signed Date 19/10/2015

Philip J. van Eyk
I aided the candidate in the processing of the data and evaluated the final version of the manuscript.

Signed Date 16/10/15

Rocky de Nys
I coordinated the cultivation of biomass for the experiments and evaluated the final version of the manuscript.

Signed Date 22/10/15

Oskar Karlström
I aided the candidate in the processing of data and evaluated the final version of the manuscript.

Signed Date 21/10/2015

David M. Lewis
I supervised the candidate, coordinated the cultivation of biomass for the experiments, and evaluated the final version of the manuscr

Signed Date 27/10/15

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Combustion Behavior of Algal Biomass: Carbon Release, Nitrogen Release, and Char Reactivity

Daniel J. Lane,[†] Peter J. Ashman,*[,†] Maria Zevenhoven,[‡] Mikko Hupa,[‡] Philip J. van Eyk,[†] Rocky de Nys,[§] Oskar Karlström,[‡] and David M. Lewis[†]

[†]School of Chemical Engineering, University of Adelaide, Adelaide, South Australia 5005, Australia

[‡]Process Chemistry Centre, Åbo Akademi University, Piispankatu 8, 20500 Turku, Finland

[§]School of Marine and Tropical Biology, James Cook University, Townsville, Queensland 4811, Australia

ABSTRACT: Recent focus on algae biomass as an alternative energy source can be attributed to building pressure for conservation of dwindling fossil fuels and reduced greenhouse gas emissions. Both micro- and macroalgae have many advantages over terrestrial plants, including typically faster growth rates and, therefore, higher rates of carbon fixation. This paper reports the combustion characteristics of a species of microalgae and two species of macroalgae under conditions that are relevant for the large-scale use of biomass for heat and other products. The tested species were *Tetraselmis* sp. (marine microalgae), *Derbersia tenuissima* (marine macroalgae), and *Oedogonium* sp. (freshwater macroalgae). Two variants of *Oedogonium* were tested. One variant was cultivated using standard nutrient additions, and the other variant was starved of essential nutrients. Carbon conversion to CO and CO_2 and the release of N as NO were determined for the algae by oxidizing fixed-bed samples of each alga in air at 800 and 1000 °C. The gasification reactivity of the chars was also characterized by gasifying samples of each alga in a thermobalance in pure CO_2 (1 atm) at 800 °C, following *in situ* devolatilization of the algal samples. Carbon conversion to CO and CO_2 exceeded 84% for all of the tested algae. Most of the fuel C was released during fuel devolatilization, consistent with the proximate analysis for these fuels. Nitrogen conversions to NO ranged between 6 and 12 g of N/100 g of fuel N for *Tetraselmis*, 6−9 g of N/100 g of fuel N for *Derbersia*, and 11−21 g of N/100 g of fuel N for the two *Oedogonium* variants, with NO emissions occurring mainly during devolatilization, in most cases. Chars produced from samples of macroalgae were much more reactive than the chars from the microalgae, most likely because of the inhibitory effects on mass transfer caused by the very high ash content of the sample used in the present study. The reactivities of all chars increased at high char conversions.

1. INTRODUCTION

Declining fossil fuel reserves and concerns regarding both future fuel security and the environmental impacts associated with greenhouse gas emissions provide strong motivation to develop alternative fuel technologies based on the sustainable use of plant biomass.[1] Combustion is one possible conversion pathway to energy that is already widely used for terrestrial biomass, and this process is well-understood for many common fuels. There have been numerous investigations of the combustion behavior of terrestrial feedstocks, ranging from woody biomass[2−5] to various sources of waste-derived fuels.[6−10]

Algae have received much attention recently because these plants are promising sources of biomass, which have several advantages over terrestrial plants. Algae have excellent potential for high energy yields per unit of land area. Productivities as high as 50 g m^{-2} day^{-1} are commonly reported in the literature.[11,12] Algae can be cultivated in fresh[13] to hypersaline water,[14] and unlike other plants, its production does not require arable land.[15] Expensive nutrient inputs can also be avoided by growing algae in agricultural,[16] municipal,[17] and industrial wastewater,[18] thus avoiding direct competition for nutrients with food crops.

Any new feedstock must be adequately characterized to identify the main challenges and benefits associated with its use as a fuel, and limited work has been performed previously to characterize the combustion behavior of algae. The literature focuses mainly on a limited range of more conventional fuel analyses[13,19−27] for a small range of algae species grown under a limited range of conditions. Proximate, ultimate, ash elemental, and heating value analyses are usually performed as a first step when characterizing new fuels. The results of these fuel analyses will vary quite widely for algae from species to species and likely depend upon a range of growing conditions, including the availability of nutrients. Often the minimization of nutrient addition is a key objective in the production of algae, and this is expected to influence the fuel properties of the resultant biomass. It is an aim of this work to investigate the extent to which different levels of nutrient addition affect the combustion behavior of algae.

Algae are typically high in elemental nitrogen, with nitrogen contents usually reported between 0.8 and 4.5 wt %[20,23,27] for macroalgae and between 6.7 and 10.3 wt %[21,22,25,26] for microalgae, on a dry and ash-free (daf) basis. Nitric oxide (NO), which may be formed from fuel N, is a harmful pollutant[28] that is a precursor to photochemical smog.[29] Emissions of nitrogen oxides (NO_x) are typically highly

Special Issue: 4th (2013) Sino-Australian Symposium on Advanced Coal and Biomass Utilisation Technologies

Received: July 31, 2013
Revised: October 21, 2013
Published: October 23, 2013

ACS Publications © 2013 American Chemical Society

dx.doi.org/10.1021/ef4014983 | *Energy Fuels* 2014, 28, 41−51

regulated[28] and have motivated[28] a vast amount of research aimed at understanding the conversion of fuel-bound N, which at low temperatures is generally the dominant contributor to NO_x emissions.[28] There have been numerous investigations into the release of fuel N from coal[30,31] and from terrestrial biomass,[32−35] and these show that mechanisms of NO_x formation differ depending upon whether fuel N is released during devolatilization or during char oxidation; thus, in practical systems, effective control measures to reduce NO_x emissions will depend upon the degree of partitioning between volatile N and char N. Ross et al.[20] compared the decomposition of six macroalgae to three different types of terrestrially sourced biomass during flash pyrolysis using thermogravimetric analysis (TGA), differential thermal analysis (DTA), and pyrolysis−gas chromatography−mass spectrometry (Py−GC−MS). They reported a greater release of nitrogenous compounds from the macroalgae and suggested that the fate of these compounds could be problematic in combustion systems. Limited work has been performed to understand the release of nitrogen during the combustion of algae.

Fuel reactivity affects the extent of fuel conversion in industrial combustion and gasification reactors and, therefore, is an important element of fuel characterization. When a solid fuel particle is fed to an industrial reactor, volatile components in the organic matter are released during pyrolysis, while the residual char is converted via much slower heterogeneous reactions with gas-phase reactants. The reactivity of the residual char depends upon not only the devolatilization conditions but also the intrinsic nature of the fuel. Furthermore, the performance of the combustion process will be strongly influenced by the relative amounts of volatiles and char. Terrestrial biomass is typically high in volatile matter,[36] and therefore, most of the carbon in the fuel is released during devolatilization. A similar behavior could be expected from algae given the high volatile matter contents reported in the literature for these fuels (58−84 wt %, daf).[20,23,24] A few experimental studies[20,37] have investigated the decomposition of algae during combustion; however, they all used slow heating rates, which poorly resemble conditions inside industrial reactors where heating of the fuel particles is rapid. No studies have been performed to track the conversion of carbon during algae combustion.

The reactivity of the residual char is especially important in determining the total conversion of carbon. There have been numerous studies focusing on the reactivity of terrestrial biomass chars and the factors that contribute to their reactivity. It is well-known from experience gasifying chars from coal[38,39] and terrestrial biomass[40,41] that the ash plays a key role in determining the reactivity of the char as well as influencing other operational factors, such as fouling,[42] during combustion and gasification. Ash interactions with the surrounding gaseous environment and with the char can act to catalyze or suppress char reactivity.[40] Algae typically contain large amounts of ash[19−21,23,24] and usually contain significant levels of Na, K, Ca, Mg, and Si,[20,23] and the alkali metals, in particular, are known to catalyze char gasification.[38,40,41] The alkaline earth metals have also been reported[38,39] to play a catalytic role but to a lesser extent than the alkali metals.[39] Silicon, on the other hand, has been reported to inhibit char gasification through the formation of inactive alkali silicates.[40] The overall catalytic influence of the ashes is likely to depend upon the balance of the main ash-forming elements in algae. Kirtania et al.[43] compared the gasification reactivity of *Chlorella* sp., a species of microalgae, to that of a commercial wood mix by monitoring weight loss during the gasification of two chars prepared from these two fuels. The chars were prepared in both an entrained flow reactor and a thermogravimetric analyser with two different gasifying agents and at two different temperatures. They found[43] chars prepared from the wood mix to be more reactive than the microalgae chars under most conditions. No other studies have been performed to characterize the reactivity of algal chars or understand how reactivity varies between species and with different growth conditions.

Therefore, the aim of this study was to characterize the combustion behavior of algal biomass. The specific objectives were to characterize the release of fuel N, the conversion of carbon, and the gasification reactivity of the chars for a range of algae species and different nutrient addition strategies.

2. EXPERIMENTAL SECTION

2.1. Algae Species. A diverse range of algae types were selected for this work to partly assess the variability in the combustion behavior of algal biomass for different types of species with different growing conditions. The experimental framework included micro- and macroalga species, freshwater and marine species, and two variants of the same species grown under different nutrient addition regimes. One species of microalgae (*Tetraselmis* sp.) and two species of macroalgae (*Derbesia tenuissima* and *Oedogonium* sp.) were studied in this work. In addition, two variants of *Oedogonium* were studied. One variant was cultivated using standard nutrient additions, and the other variant was starved of essential nutrients.

The *Tetraselmis* biomass (hereafter referred to as "Tet") used in this work was grown in an outdoor 20 m^2 raceway pond. The culture was grown in seawater and harvested every second day by electro-flocculation followed by centrifugation. The electroflocculation process involves the application of an electric current to sacrificial aluminum electrodes, which supply ions required for flocculation. The flocs, which are bubbled to the surface of the water column by gas bubbles formed at the electrodes, are then collected by skimming. The product biomass from each harvest was frozen prior to storage. Before use, samples were thawed and then oven-dried (45 °C) to a moisture content of less than 10 wt %. While individual *Tetraselmis* cells are of the order of 10 μm in size,[44] during drying, the cells aggregate to form brittle clusters up to 20 mm in size.

The *Derbersia* biomass, *D. tenuissima* (Chlorophyta, Bryopsidales) (hereafter referred to as "Deb"), was cultured in 2500 L tanks at James Cook University (JCU), Townsville, Queensland, Australia. The tanks were stocked at 1 g L^{-1} in filtered seawater (3.5 wt %) with f/2 media and harvested every 7 days by filtration through mesh bags (0.1 mm), which were subsequently spun dry (Fisher and Paykell). Harvested biomass was combined and washed in freshwater prior to being spun dry and then dried in a solar kiln (60 °C) to a moisture content of less than 10 wt %. The dried biomass consisted of tufts of intertwined filaments. The mean length and width of the dried filaments (±1 standard deviation) were measured using an optical microscope as 7.6 ± 2.9 and 0.026 ± 0.004 mm, respectively.

The *Oedogonium* biomass (*Oedogonium* from the Crispum group[13]) was cultured in 15 000 L rectangular tanks at JCU, Townsville, Queensland, Australia. The tanks were stocked at 0.5 g L^{-1} in dechlorinated water with microalgae food (MAF) culture media (0.1 g L^{-1}) and harvested after 7 days by filtration through mesh bags (0.1 mm), which were subsequently spun dry (Fisher and Paykell). This high nitrogen biomass (hereafter referred to as "OD + N") was divided, and a proportion was retained and air-dried until the moisture content was less than 10 wt %. The remaining *Oedogonium* biomass was stocked at an initial density of 0.5 g L^{-1} into 2500 L tanks with bore water without the addition of nutrients. This low nitrogen biomass (hereafter referred to as "OD − N") was harvested after 7 days as above and air-dried until the moisture content was less than 10 wt %. The dried *Oedogonium* biomass consisted of tufts of intertwined

dx.doi.org/10.1021/ef4014983 | *Energy Fuels* 2014, 28, 41−51

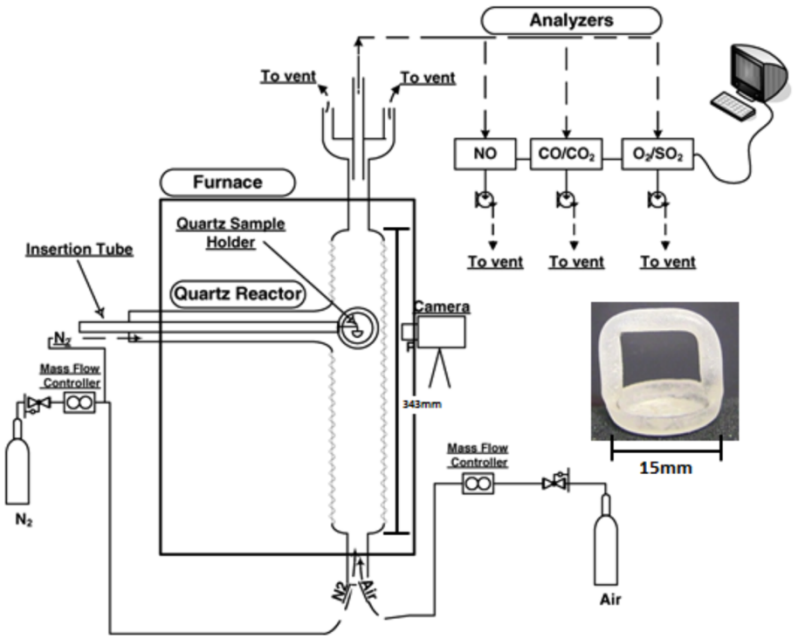

Figure 1. Quartz furnace setup at Åbo Akademi University (taken from Giuntoli et al.[33]) and (inset) photograph of one of the quartz sample holders.

filaments, similar in appearance to Deb. The mean length and width of the dried filaments (±1 standard deviation) were measured using an optical microscope as 4.6 ± 0.9 and 0.03 ± 0.002 mm, respectively.

Representative samples of each species of macroalga were milled using a centrifugal knife mill and then sieved to pass through a 1 mm screen to obtain particles that were approximately similar in size to the microalgae particles. The dried microalga was also sieved through a 1 mm screen to remove coarse particles. The action of sieving alone was sufficient to break most of the coarse microalgae clusters. The resultant biomass was split by cone and quartering to obtain smaller sample sizes for each analysis.

2.2. Experiments. Conventional fuel analyses were performed on each alga sample. Ultimate, proximate, ash elemental, and heating value analyses were performed externally by Belab AB and ALS Scandinavia (accredited laboratories in Sweden) according to Swedish standards. Elemental C, H, and N were determined according to SS-EN 15104:2011/15407:2011. Elemental O was calculated by difference. Elemental S and the ash analyses were determined using modified United States Environmental Protection Agency (U.S. EPA) methods 200.7 [inductively coupled plasma−atomic emission spectrometry (ICP−AES)], 200.8 [inductively coupled plasma−mass spectrometry (ICP−MS)], and 200.8 [inductively coupled plasma−sector field mass spectrometry (ICP−SFMS)]. Moisture and volatile matter contents were determined according to SS028113-1 and SS-EN 15148:2009/15402:2011, respectively. Fixed carbon was calculated by difference. Heating values were determined according to 14918:2010/15400:2011.

2.2.1. Carbon and Nitrogen Release Experiments. The carbon release as CO and CO_2 and N release as NO were characterized by oxidizing samples of the algae in a lab-scale quartz furnace at Åbo Akademi University.

2.2.1.1. Apparatus Setup. A schematic of the quartz furnace setup is shown in Figure 1. The setup consisted of an insulated quartz tube reactor (inner diameter of 44 mm) connected to a series of commercial gas analysers. A chemiluminescence analyzer was used for NO measurement and a non-dispersive infrared analyzer for simultaneous CO and CO_2 measurements. The setup did not allow for the measurement of light hydrocarbons (e.g., CH_4) or for the measurement of nitrogenous species other than NO. A view port at the front of the reactor, designed for video recording, allowed for visual observation. Samples were fed into the reactor using a quartz sample holder suspended from the end of a quartz insertion probe. The feeding system was designed such that the sample could be preserved in N_2 and maintained at close to ambient temperature while conditions inside the furnace stabilized. Once the conditions inside the furnace had stabilized, the sample was inserted into the reactor within a fraction of a second. Dry air and N_2 were fed into the front, bottom, and side of the reactor to create the desired gas atmosphere. Mixing of the gases occurred inside the reactor. Mass flow controllers were used to control the flows of each gas to the different locations. The total gas flow into the reactor was kept constant at 220 L h^{-1} [standard temperature and pressure (STP)]. This flow rate allowed for sufficient time for the incoming gases to be heated to the reactor temperature. It also resulted in a relatively short transfer time of the product gases between the reactor and the gas analysers, which was estimated to be around 4 s. Four externally controlled electric heating elements were used to heat the furnace. The heating elements were distributed evenly around the outside of the quartz tube to provide uniform heating. A K-type thermocouple, located just beneath the base of the quartz tube, was used for temperature measurement inside the reactor.

2.2.1.2. Procedure. Samples of milled alga (10−15 mg) were loaded onto the quartz sample holder to create a thin layer of particles with a depth no greater than 2 mm. The samples were oxidized at the following three sets of conditions: 3% O_2 and 800 °C, 10% O_2 and 800 °C, and 10% O_2 and 1000 °C. The concentrations of NO, CO, CO_2, and O_2 in the product gases from the furnace were measured during each test. Tests were repeated at least 4 times at each condition to assess the reproducibility of the measurements. The tests showed reasonable reproducibility: the relative standard deviations of the integrals of the CO + CO_2, NO, and O_2 curves were usually within 6, 11, and 5%, respectively. The average integral of the measured signals was calculated to determine the conversion of fuel C to CO and CO_2 and the total release of fuel N as NO. A representative signal from each test was selected to partition the total release of carbon and fuel N as NO between fuel devolatilization and oxidation of the residual char. The representative signal was deconvolved using a standard Matlab routine, which used the residence time distributions (RTDs) of the

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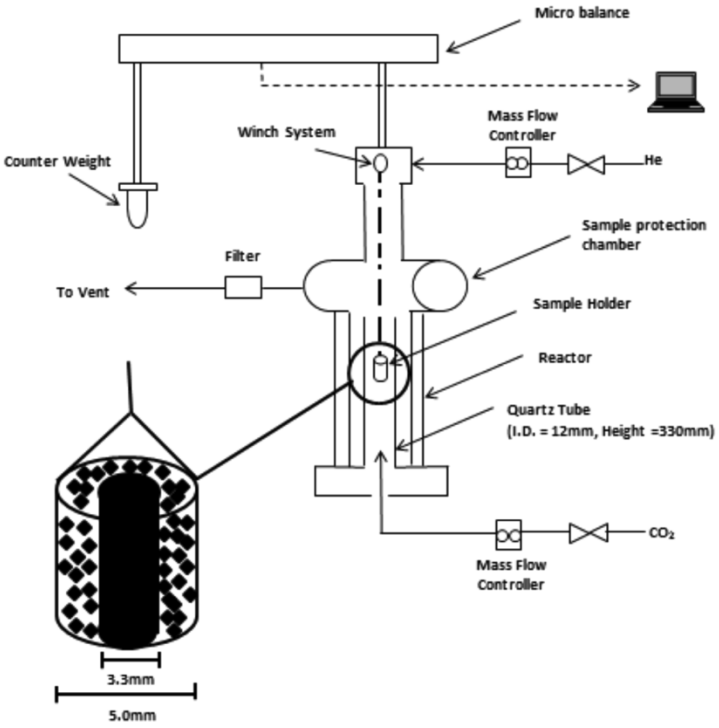

Figure 2. Simplified schematic of the experimental setup used in the char reactivity experiment.

Table 1. Proximate, Ultimate, and Heating Value Analyses of the Tested Algae[a]

	Tet	Deb	OD + N	OD − N	spruce wood[36,45]	switchgrass[36,46]	chicken manure[47]	sewage sludge[36,48]
Proximate (wt %)								
moisture[b]	7.9	6.6	6.2	8.2				
VM[c,d]	41.9	74.8	77.3	77.2	81.1	80.4	67.9	48.1
FC[e,d]	<1.0	15.1	14.7	6.1	18.3	14.5	5.5	5.7
ash	64.4	10.1	8.0	16.7	0.5	5.1	26.6	46.2
Ultimate (wt %)[f]								
C	42.1	52.6	49.1	47.4	52.3	49.7	54	50.9
H	8.7	7.2	6.8	6.8	6.1	6.1	5.6	7.3
N	6.7	7.6	4.5	1.5	0.3	0.7	8	6.1
O	35.4	30.9	39.2	44.1	41.2	43.4	30.9	33.4
S	6.9	1.3	0.12	0.20	0.1	0.11	1	2.33
higher heating value (MJ/kg)[f]	15.5	21.7	19.36	17.39	20.1	18.6	18.1	20.8

[a]The analyses are compared to the analyses of terrestrial biomass reported in the literature. [b]After drying. [c]Volatile matter. [d]Dry basis. [e]Fixed carbon. [f]Dry and ash-free basis.

measured gas species as an input. Step tests were performed with CO, CO_2, and NO to determine RTDs.

2.2.2. Char Reactivity Experiment. The gasification reactivities of the algal chars were characterized by gasifying samples of each alga in a pure CO_2 environment (1 atm) at 800 °C in a thermogravimetric analyser at Åbo Akademi University. A simplified schematic of the TGA setup is shown in Figure 2. The method used was adapted from a method developed by Moilanen[40] to characterize the reactivity of terrestrial biomass chars. The method involves *in situ* drying and devolatilization of the fuel sample, simulating conditions in an industrial reactor. Samples of each alga (35−182 mg) were packed into an inconel sample holder, which was then held above a quartz tube furnace in an inert water-cooled gas chamber, while the furnace was heated to 800 °C. The sample holder consisted of a solid cylinder surrounded by porous wire mesh. The sample was packed into the annular region between the wire mesh and the cylinder. The sample layer was sufficiently thin (<1.7 mm) to promote good contact with the gasifying agent. Once the furnace temperature reached 800 °C, the sample was lowered into the furnace using an electrically operated winch. A total of 27 s was required to lower the sample into the furnace and for the balance to stabilize. The sample weight was recorded from 27 s up until steady-state weight was obtained with a sampling interval of 0.5 s. A K-type thermocouple located just beneath the sample holder was used to monitor the furnace temperature. Helium was fed at a rate of 2.2 L min^{-1} to the inert chamber and preheated CO_2 at a rate of 2.0 L min^{-1} to the bottom of the furnace. Gas flows were controlled using mass flow controllers.

The obtained weight loss curves were used to calculate the rate profiles for char gasification. The rate profiles show the instantaneous reaction rate as a function of char conversion. In this work, the instantaneous rate was defined as the rate of mass change of the char divided by the mass of residual ash-free char and char conversion was

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defined as the reacted part of the ash-free char. The instantaneous rate, r'' (min^{-1}), was calculated according to eq 1, and char conversion, X (%), was calculated according to eq 2

$$r'' = \frac{-(m_i - m_{i-1})}{(t_i - t_{i-1})(m_i - m_F)} \quad (1)$$

$$X = 1 - \frac{m_i - m_F}{m_0 - m_F} \quad (2)$$

where m_i is the sample mass at time t_i, m_{i-1} is the sample mass at time t_{i-1}, m_F is the minimum sample mass, and m_0 is the initial mass of char, which was approximated by the sample mass at the time corresponding to a sudden reduction in the slope of the weight loss curve. This point is assumed to correspond to the end of fuel devolatilization and the onset of char gasification.

3. RESULTS AND DISCUSSION

The results from the proximate, ultimate, and heating value analyses are presented in Table 1, and the results from the ash elemental analyses are presented in Table 2. Data for four terrestrial biomass fuels, viz., spruce wood,[36,45] switchgrass,[36,46] chicken manure,[47] and sewage sludge,[36,48] have also been included in Table 1 for comparison. The *Derbersia* biomass (Deb) and the high-nitrogen *Oedogonium* biomass (OD + N) have the highest fixed carbon (FC) of the tested algae on a daf basis with 16.8 and 16.0 wt %, respectively. The ratio of volatile matter (VM) to FC in Deb and OD + N are approximately 5 and are typical of that reported for grasses.[36,46] The low-nitrogen *Oedogonium* biomass (OD − N) contained similar proportions of FC and VM to chicken manure and approximately half as much FC as OD + N on a daf basis. The lack of essential nutrients available to OD − N during its growth has likely caused changes to the biochemical structure of the plant material, which has resulted in a greater proportion of the organic matter being released as VM during devolatilization. The *Tetraselmis* biomass (Tet) was reported to contain less than 3 wt % FC (daf) based on the standard analytical method used for this analysis. This value is very low and is much lower than what is reported for terrestrial plants in a recent overview[36] of the chemical composition of over 80 types of biomass. Furthermore, our own determination of the FC content using a thermogravimetric analyser, albeit under different conditions to the standard method, showed the FC content of the Tet sample to be approximately 9 wt %, which is also supported by observations from our own combustion experiments. It is possible that the discrepancy between the two analyses is due to some organic material remaining unconverted in the standard method. The Tet sample has a very high ash content (64.4 wt %), and it is possible that mass transfer resistance caused by the formation of a substantial ash layer in the Tet sample prevents the complete conversion of the Tet sample. Nevertheless, the FC content of Tet is clearly lower than that measured for other algae and can be attributed to the structural simplicity of microalgae.

Table 2. Ash Elemental Analyses for the Tested Algae

	mg/kg of dry biomass			
	Tet	Deb	OD + N	OD − N
Na	110000	14300	2280	2890
K	8090	9250	14900	21800
Ca	19400	2600	2680	22700
Mg	19500	5850	2920	10100
Si	5910	3470	10400	12600
P	1930	4530	6840	2130
Al	65100	113	710	793
Fe	996	833	2280	627
Ti	81.4	12.6	28.4	29.6
Mn	43.1	38	279	216
Cl	182000	19800	2380	7930

The ash contents of the tested algae were in the range of 8.0−64.4 wt % on a dry basis (db) and varied substantially between species. Differences in the growth and harvesting processes used to produce the different types of algae biomass are expected to account for much of this variation. Tet had the highest ash content (64.4 wt %) followed by OD − N (16.7 wt %), Deb (10.1 wt %), and then OD + N (8.0 wt %). The difference in the ash contents of OD + N and OD − N is attributable to the final culture of OD − N occurring in bore water, which was high in carbonates, resulting in internal accumulation of salts and, therefore, ash. The composition of ashes from both the marine algae, Tet and Deb, are dominated by NaCl originating from the seawater in which they were cultured. The lower ash content of Deb compared to Tet is due to Deb being washed with freshwater prior to drying. The extremely high ash content of the Tet sample is attributed to the hypersaline growth conditions but also the harvesting and drying processes employed. The electroflocculation harvesting process, which causes flocculation and flotation of microalgae, may also recover other fine materials present in the pond. While this biomass sample was partially dewatered using centrifugation, the Tet samples were finally dried by evaporation, resulting in a concentration of soluble inorganic matter associated with the water phase of the wet biomass.

The elemental composition of OD + N and OD − N (Table 1) was similar and also similar to that of switchgrass[36] on a daf basis, except that OD + N contained higher levels of N. Deb had a higher C content and significantly lower O content (8−13%) than the two variants of *Oedogonium*. Thus, Deb had the highest calorific value, despite it containing more ash than OD + N. The elemental composition of Deb was similar to that of chicken manure[47] on a daf basis. Tet contained high levels of both N and S and contained the least C of the algae tested. The S levels in Tet are 4−13 times higher than those reported in the literature[21,22,25,26] for microalgae laboratory cultures. It is suspected but not confirmed that extraneous sulfate ions were incorporated within the biomass during the electroflocculation harvesting process. Deb also had a higher S content (1.3 wt %) than the two *Oedogonoium* variants (0.1−0.2 wt %).

Nitrogen levels in the tested algae ranged between 1.5 and 7.6 wt % (daf). The N content of Tet was 6.7 wt %, which is at the lower limit of that reported in the literature[21,22,25,26] for microalgae. The high levels of N in microalgae are attributed to the ability of microalgae to store excess N as nitrate in their vacuoles.[49] OD − N contained 1.5 wt % N, the lowest of all of the algae tested here, and this value is typical of grasses[36] and herbaceous crops.[36] OD + N contained 4.5 wt % N, which is 3 times more than that in OD − N. This was expected given that OD − N was starved of N during cultivation. The highest N content was measured for Deb (7.6 wt %, daf). Given the high levels of N in Deb and OD + N, it is likely that these two macroalgae stored excess N to what is needed for essential biological functioning (luxury uptake). In contrast, it is expected that a large part of the N in OD − N was incorporated into essential organic molecules, such as proteins.

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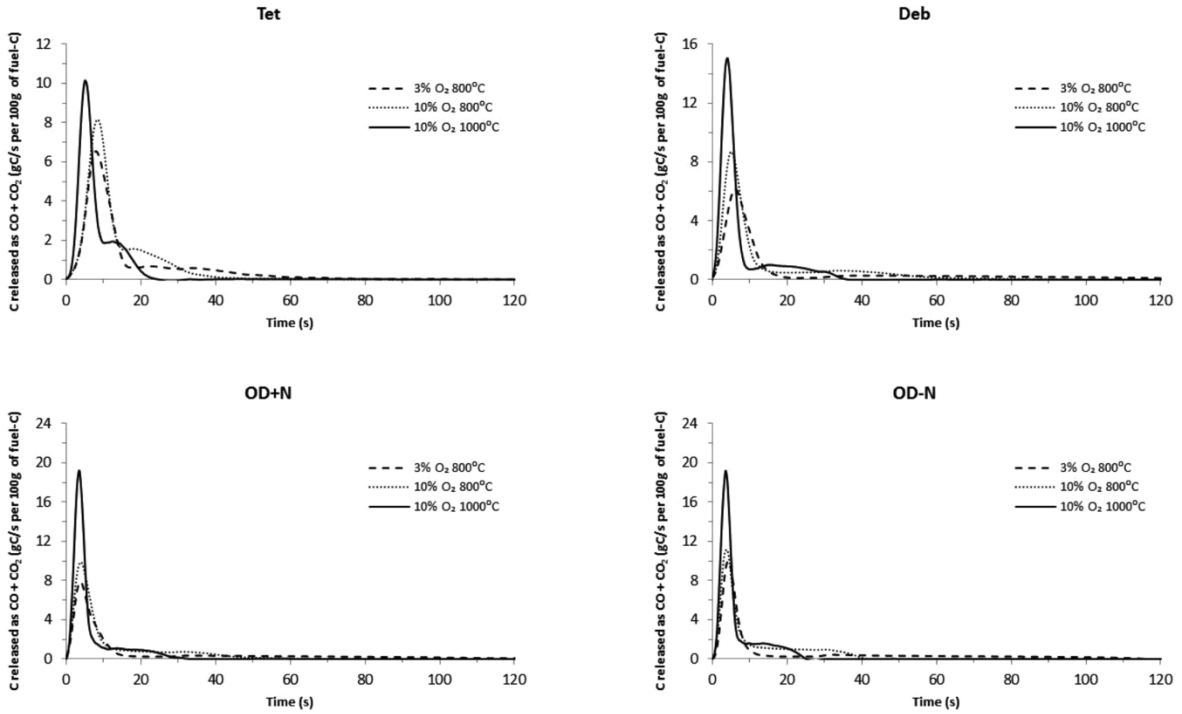

Figure 3. Carbon released as CO and CO_2 from the tested algae in a quartz tube furnace. Release profiles obtained at 10 vol % O_2 and 800 °C are compared to release profiles obtained at 3 vol % O_2 and 800 °C and at 10 vol % O_2 and 1000 °C.

3.1. Carbon Release. Figure 3 shows the C conversion to CO and CO_2 for each of the tested algae in the quartz tube furnace. The profiles all consist of an initial peak followed by a tail. We interpreted the initial peak to correspond to fuel devolatilization and combustion of the volatiles and the tail to correspond to oxidation of the residual char. Increasing the furnace temperature from 800 to 1000 °C had a similar effect on the release profiles for all of the tested algae. The initial peaks were both higher and narrower at 1000 °C than at 800 °C, indicating an increase in the amount and rate of C conversion to CO and CO_2 during devolatilization at the higher temperature. The tails were shorter at 1000 °C and started from higher up on the peak, indicating an increase in the rate of char oxidation as well as greater overlap between devolatilization and char oxidation. The times necessary for carbon burnout were in the order of 25−35 s at 1000 °C and 40−90 s at 800 °C. Decreasing the oxygen partial pressure from 10 to 3 vol % resulted in a significant increase in the carbon burnout times for the tested algae, as indicated by the increase in tail lengths at the 3% O_2 and 800 °C reaction conditions. Burnout times were in the order of 80−160 s at 3% O_2 and 800 °C. As expected, char burnout times for Deb and OD + N, the two fuels with the highest FC contents, were greater than the burnout times for Tet and OD − N.

Figure 4 shows the C conversion to CO and CO_2 from the tested algae. Carbon conversion was determined by comparing the total C emitted as CO and CO_2 in the quartz tube furnace to the initial fuel C content reported in Table 1. As expected, the total release of carbon was proportional to the initial fuel C content. The C mass-balance closures were all within 84%. Unreacted light hydrocarbons most likely accounted for the balance, and therefore, for higher oxygen partial pressure and

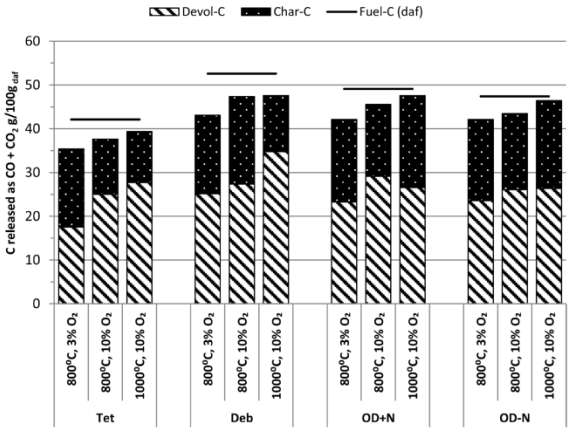

Figure 4. Carbon conversion to CO and CO_2 from the tested algae as determined by oxidizing algae samples in a quartz tube furnace. Fuel C contents were taken from Table 1. Data are on a daf basis.

temperature, the extent of light hydrocarbons being oxidized to CO and CO_2 is increased and a higher extent of carbon conversion to CO and CO_2 is measured. Figure 4 also shows the partitioning of carbon between the devolatilization and char oxidation stages. For these data, we have determined the transition between devolatilization and char oxidation based on an extrapolation of the initial devolatilization peak; the area under this peak was then used to determine the amount of C released as CO and CO_2 during devolatilization. The total release of carbon as CO and CO_2 during char oxidation was then determined as the difference between total carbon release

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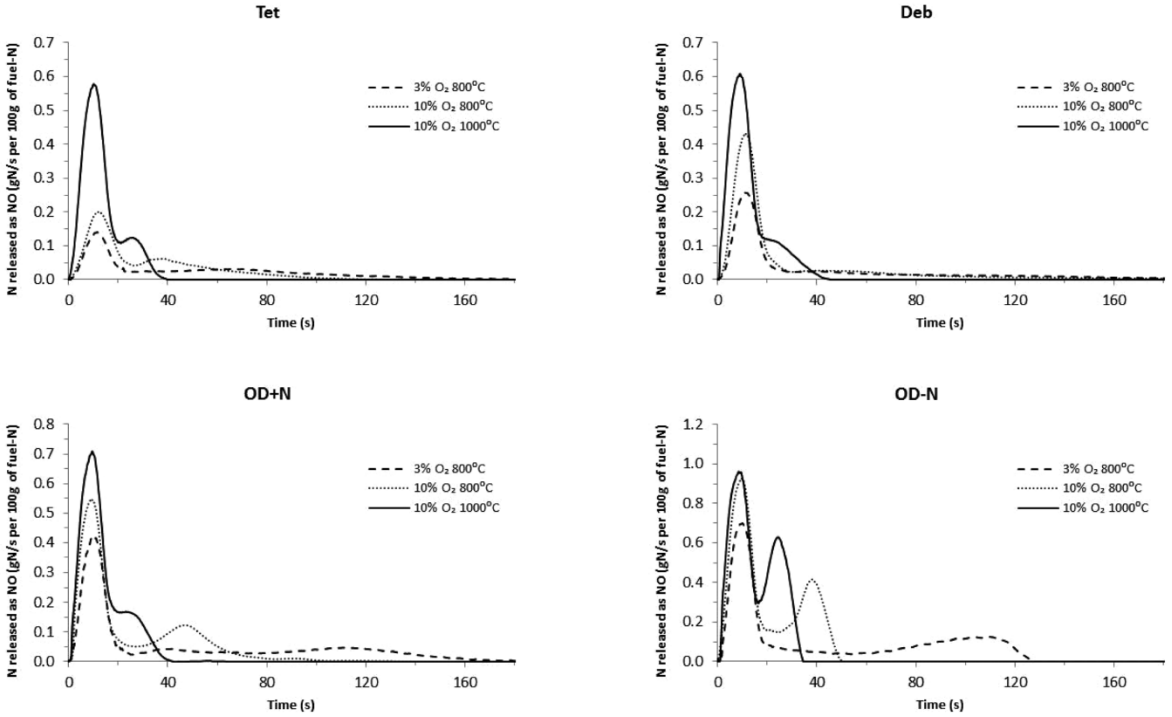

Figure 5. Nitrogen released as NO from the tested algae in a quartz tube furnace. Release profiles obtained at 10 vol % O_2 and 800 °C are compared to release profiles obtained at 3 vol % O_2 and 800 °C and at 10 vol % O_2 and 1000 °C.

(on the basis of the total area under the curve) and the total carbon release during devolatilization. The majority (53−73%) of the C released as CO and CO_2 was emitted during devolatilization. This is expected given the high VM/FC ratios of the tested alga.

Reducing the oxygen partial pressure from 10 to 3% O_2 resulted in a slight decrease in the proportion of C converted to CO and CO_2 during devolatilization for all of the tested algae. This is again attributed to unconverted light hydrocarbons released during devolatilization. Increasing the furnace temperature from 800 to 1000 °C affected the C partitioning in different ways for the different algae. For Tet and Deb, an increasing temperature resulted in an increase in the proportion of carbon released as CO and CO_2 during devolatilization, which is expected because of the known dependence of the volatile yield on the temperature. For OD + N and OD − N, an increasing temperature had the opposite effect on the C partitioning, and the reason for this is unclear. It is possible that there was some removal of carbon by the formation of soot at the higher temperature because of the increased rate of devolatilization.[33]

3.2. Nitrogen Release. Figure 5 shows the N released as NO from the tested algae in the quartz tube furnace. Similar to the carbon release profiles, the NO release profiles all consisted of an initial peak, presumably corresponding to fuel devolatilization and the homogeneous reaction of the released volatiles, and a tail, presumably corresponding to oxidation of the residual char. The initial peaks from the different algae vary in both height and width but, otherwise, are similar in shape. The shape of the tails on the other hand vary depending upon the alga and the reaction conditions, possibly indicating different release mechanisms during char oxidation. The profiles corresponding to OD + N, OD − N, and to a lesser extent, Tet all contained at least one secondary peak. It is suspected that the secondary peaks are a result of changes in the char structure during char oxidation. It is possible that the changes in the char structure expose nitrogen-rich zones of the char matrix. While there were some small differences in the temporal responses of the gas analysers used to measure CO, CO_2, and NO, it is still clear that nitrogen burnout took longer than carbon burnout, indicating selective depletion of fuel C over fuel N. Nitrogen burnout times were of the order of 35−45 s at 10% O_2 and 1000 °C, 50−220 s at 10% O_2 and 800 °C, and 130−240 s at 3% O_2 and 800 °C. Nitrogen burnout was fastest for OD − N, which contained the least fuel N, and was the slowest for Deb, the algae with the most fuel N. Nitrogen burnout times for Tet and OD + N were between those of OD − N and Deb. Nitrogen burnout took slightly longer for Tet than for OD + N, even though OD + N contained more fuel N than Tet on a dry basis. This is likely a result of mass transfer limitations in the Tet sample caused by its high ash content.

Figure 6 shows the N conversions to NO for the tested algae expressed as a proportion of the available fuel N. Nitrogen conversion to NO was determined by comparing the total amount of N emitted as NO in the quartz tube furnace to the initial fuel N content reported in Table 1. Emissions of nitrogenous species other than NO were not measured. NO emissions ranged between 0.4 and 0.8 g of N/100 g for the tested algae, corresponding to fuel N conversion to NO of 5.9−21.2% (Figure 6). The balance of fuel N was most likely emitted as other gas-phase nitrogenous species, including, for example, N_2, NH_3, HCN, and N_2O. On average, Deb emitted

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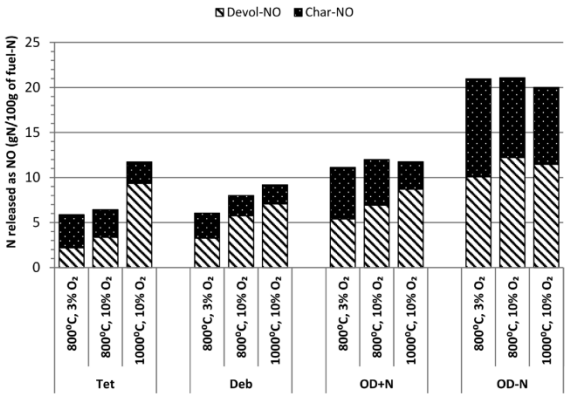

Figure 6. Nitrogen conversion to NO for the tested algae as determined by oxidizing algae samples in a quartz tube furnace. Fuel N contents were taken from Table 1.

the most NO (0.53 g of N/100 g, db) of the tested algae, followed by OD + N (0.48 g of N/100 g, db), OD − N (0.26 g of N/100 g, db), and then Tet (0.19 g of N/100 g, db). NO emissions from the macroalgae samples were found to increase with increasing fuel N content; however, the increase was not proportional to the increase in fuel N content. In fact, N conversion to NO diminished with increasing fuel N content on a daf basis. This trend may be attributed to thermal $deNO_x$,[33] involving the homogeneous reduction of NO by NH_3 to N_2 and H_2O.[50] Giuntoli et al.[33] explained that an increasing fuel N content leads to an increase in the concentration of NH_i radicals released during devolatilization, which results in an increase in the extent of NO reduction by thermal $deNO_x$. The same trend has been reported during the combustion of various types of terrestrial biomass;[32−34] however, this is less apparent in coal combustion,[32,51] in which N conversion to NO seems relatively insensitive to the amount of fuel N. The results for the macroalgae (OD + N, OD − N, and Deb) are compared to the NO emission data reported by Giuntoli et al.[33] and Winter et al.[34] for terrestrial biomass in Figure 7. Winter et al.[34] measured NO emissions from spruce wood, alder wood, peat, and malt waste in a fluidized-bed reactor. Giuntoli et al.[33] measured NO emissions from five waste fuels in the same reactor used in the present study. The conversions reported by Winter et al.[34] are lower than the conversions reported in this study and by Giuntoli et al.;[33] however, this is likely to be due to the different reactor configurations.

Nitrogen released as NO from Tet was the most sensitive to changes in the temperature of all of the tested algae. At 800 °C and 10 vol % O_2, only 5.9% of the fuel N in Tet was converted to NO. The NO emission levels from Tet were 20% lower than the levels emitted by OD + N at 800 °C, even though the Tet sample contained nearly 50% more fuel N than OD + N on a dry basis. At 1000 °C, the amount of N released as NO from Tet almost doubled and exceeded that released by OD + N by approximately 50%. By comparing the heights of the initial peaks from the NO emission profiles for Tet at 800 and 1000 °C at 10 vol % O_2 in Figure 5, it can be seen that the increase in NO emissions at 1000 °C occurred during devolatization rather than during char oxidation. The N partitioning (as determined using the same method used to determine the C partitioning) for Tet shifted from 53% devolatile NO/47% char NO at 800 °C to 80% devolatile NO/20% char NO at 1000 °C, as illustrated in Figure 6. The increase in the temperature had a similar effect but to a lesser extent on the N partitioning for Deb and OD + N. The NO emissions from OD − N were relatively insensitive to the change in the temperature.

The amount of N released as NO from the tested algae was found to decrease by up to 32% upon reducing the oxygen partial pressure from 10 to 3 vol % O_2. The reduction in NO

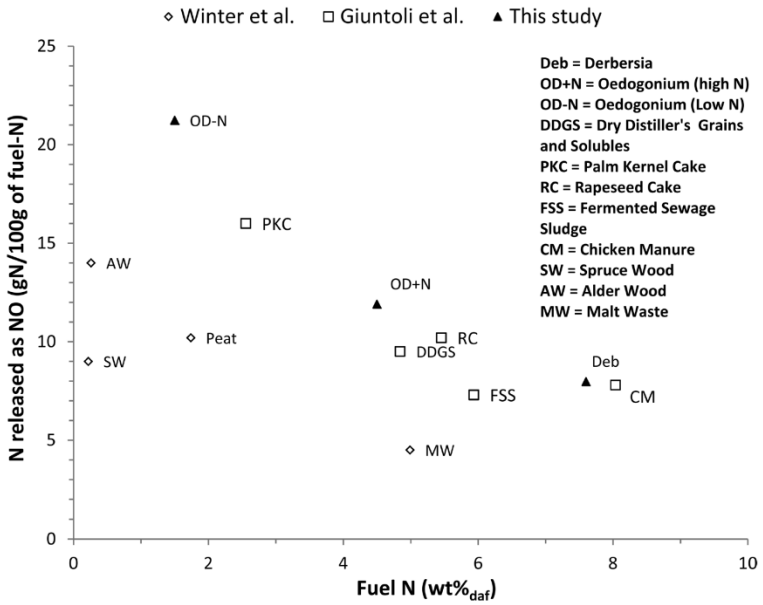

Figure 7. Fuel N conversion to NO as a function of initial fuel N content at 800 °C and 10% O_2. Data for the macroalgae samples are compared to data reported for terrestrial biomass by Giuntoli et al.[33] and Winter et al.[34]

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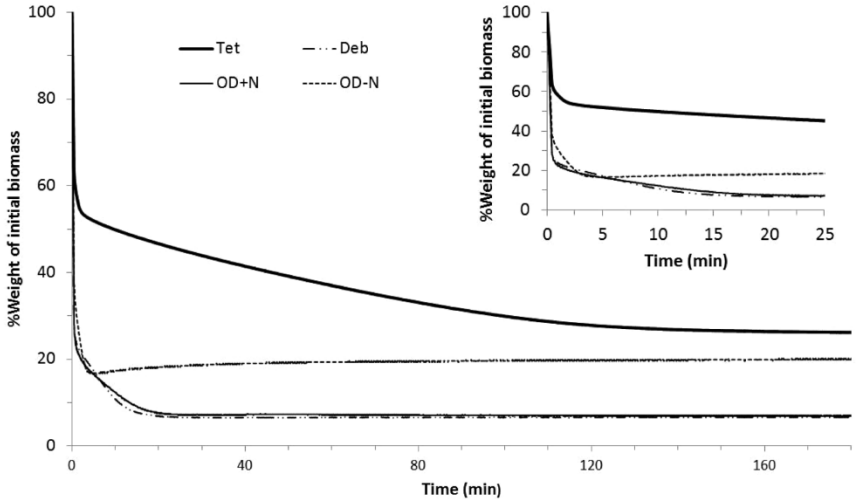

Figure 8. Gasification weight loss profiles for the tested algae at 800 °C in pure CO_2. The sudden reduction in the slope of the weight loss curves indicates the transition between fuel devolatilization and oxidation of the residual char. The inlay (small plot) shows the first 25 min of reaction.

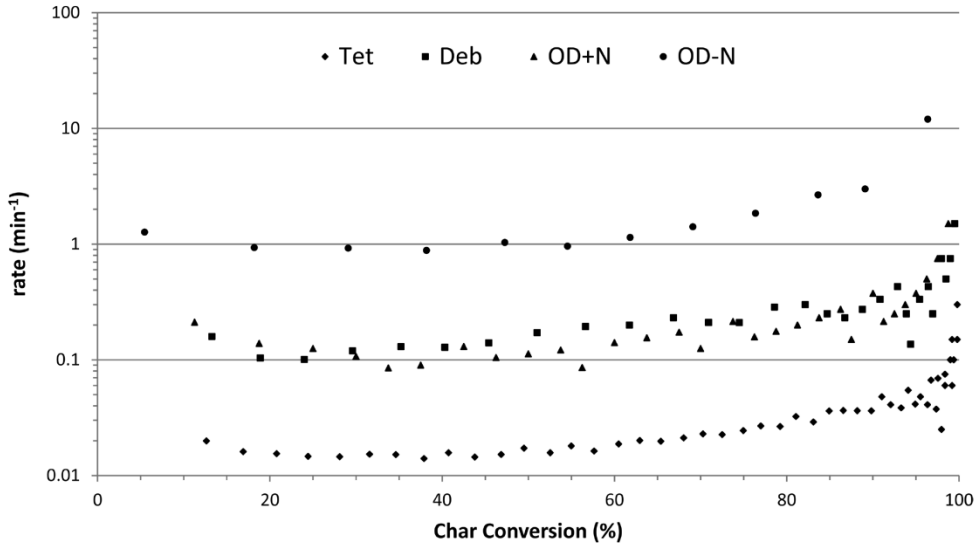

Figure 9. Char gasification rate profiles for the tested algae at 800 °C in pure CO_2. The rate profiles were calculated from the gasification weight loss curves presented in Figure 8.

emissions occurred mainly during devolatilization, and consequently, the N-partitioning shifted away from devolatilization and toward char oxidation. This change in N-release behavior is consistent with results reported in the literature for both coal and biomass.[32] Jenkins et al.[32] explained that the reduced oxygen availability at lower oxygen partial pressures leads to increased competition for oxygen between C and N, resulting in reduced availability of oxygen for NO_x formation. The NO release from OD − N was relatively insensitive to the change in oxygen partial pressure and was an exception to this finding.

3.3. Char Reactivity. The CO_2 gasification weight loss profiles for the tested algae are presented in Figure 8. Complete conversion of the chars took between 200 s and 2.5 h. Upon close inspection of Figure 8, the curve for OD − N reaches a minima of 17% at approximately 200 s and then proceeds to increase to 20% (the steady-state value) with increasing time. When calculating the instantaneous rate (r'') of char conversion for OD − N, the weight at the minima was used rather than the steady-state weight. The increase in sample weight after 200 s is most likely due to carbonate formation, resulting from the reaction of CO_2, the gasifying agent, with inorganic elements (especially calcium) in the residual char. In the first 200 s of reaction, it is likely that there was a reduced concentration of CO_2 in the gaseous environment immediately surrounding the algae particles because of the presence of pyrolysis gases. This would have reduced the potential for carbonate formation.

The char of Tet was by far the least reactive of the tested algae, as seen by comparison of the rate profiles presented in Figure 9. The rate profiles show how the instantaneous reaction

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rate changes with char conversion. The Tet char was approximately 1 order of magnitude less reactive than the chars from Deb and OD + N and 2 orders of magnitude less reactive than the OD − N char. The relatively low reactivity of the Tet char can also be seen in Figure 8. After 2 h, much of the Tet char was still unconverted, whereas the chars from Deb, OD + N, and OD − N were all more or less completely converted after 25 min. The reactivity of the Tet char is also significantly lower than that reported for *Chlorella* sp. microalgae by Kirtania et al.,[43] who found the char from *Chlorella* sp. to be more or less completely converted within 20 min.[43] Mass transfer limitations were most likely responsible for the low reactivity of the Tet char. Tet has an extremely high ash/FC ratio (>15). By comparison, the ash/FC values for the macroalgae samples and for *Chlorella* sp.[43] were between 0.5 and 2.7. It is suspected that the ash from the Tet sample formed a protective layer around the char particles, which inhibited gas contact with the char.

The chars from Deb and OD + N had similar reactivities and were approximately an order of magnitude less reactive than the OD − N char. Differences in the macroalgae ashes are likely to be largely responsible for the differences observed in the reactivities of the macroalgal chars. The overall catalytic effect of the ashes is likely to depend upon the relative proportions of the main-ash forming elements in the macroalgae, which were K, Na, Ca, Mg, Si, and Cl. OD − N, the alga with the most reactive char, contained the most alkali metals and alkaline earth metals, both of which are known to have a strong catalytic effect on char gasification.[38−41]

The rate profiles for the tested algae all follow a similar trend. The rate was found to remain relatively constant for char conversions up until about 60% and then increase by approximately an order of magnitude in the range from 60 to 100% conversion. Moilanen et al.[52] reported a similar trend from the gasification of birch wood pieces in 1 bar steam at 800 °C in an apparatus that also involved *in situ* devolatilization. Henriksen et al.[41] also found that the reaction rate increased at high conversion values during the gasification of straw chars at 800 °C. Interestingly, the reactivities of the birch wood char and straw char were of a similar magnitude to that of the chars from OD + N and Deb; however, direct comparison is difficult because of differences in the experimental setup and gas atmospheres between those experiments and the experiments reported here. Moilanen[40] proposed two reasons for an increasing reaction rate with char conversion: (i) an increasing catalyst/C ratio in the residual char with an increasing char conversion and (ii) an increasing char porosity with an increasing conversion, making more active sites available for gasification. An increasing reaction rate profile with conversion has positive implications for achieving high conversions in practical systems because complete conversion of the char particles is more likely provided that the residence times for the char particles in the reactor are sufficiently long.

A high-temperature pulverized fuel reactor may be a suitable technology for the conversion of Tet given its low char reactivity. This technology would also have the added advantage that the microalgae could be fed as a powder. However, the impact of the high ash content for Tet would need to be considered. The macroalgae on the other hand are more reactive than Tet and may be better suited in low-temperature fluidized-bed reactors.

■ CONCLUSION

The combustion of *Tetraselmis*, *Derbersia*, and two types of *Oedogonium* in a fixed bed within a quartz tube furnace showed that most of the fuel C is converted to CO and CO_2 during devolatilization, with carbon conversion exceeding 84% for all of the tested algae. Nitrogen conversions to NO in the quartz furnace ranged between 6 and 12 g of N/100 g of fuel N for *Tetraselmis*, 6−9 g of N/100 g of fuel N for *Derbersia*, and 11−21 g of N/100 g of fuel N for the two *Oedogonium* variants on a daf basis. The fraction of fuel N that was released as NO during combustion of *Oedogonium* was reduced by 43−49% by starving the alga of essential nutrients during cultivation. In most cases, NO emissions were also predominately released during devolatilization, which is consistent with the high volatile matter content for these fuels. The chars from *Oedogonium* and *Derbersia* have similar gasification reactivities and are an order of magnitude more reactive than the *Tetraselmis* char. The reactivities of these chars are similar in magnitude to that of birch wood char and straw char. The gasification reactivity of the *Oedogonium* char was increased by starving *Oedogonium* of essential nutrients during cultivation. The reactivities of the algal chars all increase at high char conversions.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: peter.ashman@adelaide.edu.au.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The characterisation work was carried out at the Process Chemistry Centre of Åbo Akademi University, Finland, within FUSEC (2011−2014), a project financed by the National Technology Agency of Finland (TEKES) and industrial partners Andritz Oy, Metso Power Oy, Foster Wheeler Energia Oy, UPM-Kymmene Oyj, Clyde Bergemann GmbH, International Paper, Inc., and Top Analytica Oy Ab. Nikolai de Martini is acknowledged for his help in the treatment of the quartz furnace data, and Luis Bezerra and Peter Backman are acknowledged for their technical support in various aspects of this work. This research was supported under Australian Research Council's Linkage Projects Funding Scheme (Project LP100200616) with our industry partner SQC Pty Ltd. The project was also supported by the Australian Government through the Australian Renewable Energy Agency (ARENA) and the Advanced Manufacturing Cooperative Research Centre (AMCRC), funded through the Australian Government's Cooperative Research Centre Scheme. Andrew Cole and Marie Magnusson are acknowledged for the support in the production of macroalgal biomass. The authors also acknowledge the support of Muradel Pty Ltd. and MBD Energy.

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Chapter 4

Paper II

Algal Biomass: Occurrence of the Main Inorganic Elements and Simulation of Ash Interactions with Bed Material

Daniel J. Lane[a], Maria Zevenhoven[b], Peter J. Ashman[a], Philip J. van Eyk[a], Mikko Hupa[b], Rocky de Nys[c], and David M. Lewis[a]

[a]School of Chemical Engineering, The University of Adelaide, Adelaide, South Australia 5005, Australia

[b]Process Chemistry Centre, Åbo Akademi University, Piispankatu 8, Turku 20500, Finland

[c]MACRO – the Centre for Macroalgal Resources and Biotechnology, and School of Marine and Tropical Biology, James Cook University, Townsville, Queensland 4811, Australia

Energy & Fuels **2014**, 28 (7), pp. 4622 – 4632.

Statement of Authorship

Publication details: Lane DJ, Zevenhoven M, Ashman PJ, van Eyk PJ, Hupa M, de Nys R, Lewis DM. Algal biomass: occurrence of the main inorganic elements and simulation of ash interactions with bed material. Energy & Fuels 2014; 28 (7): 4622-4632.

Publication status: Published

Author contributions:

By signing the Statement of Authorship, each author certifies that their stated contribution to the publication is accurate and that permission is granted for the publication to be included in the candidate's thesis.

Daniel J. Lane (Candidate)
Under the supervision of M. Zevenhoven, M. Hupa, P. J. Ashman, P. J. van Eyk, and D.M. Lewis, I designed and performed the experiments, interpreted and processed the data, and wrote the manuscript.

Signed Date 16/10/2015

Maria Zevenhoven
I supervised the candidate and aided in the design of experiments and processing of data. I also evaluated the final version of the manuscript.

Signed Date 21/10/2015.

Peter J. Ashman
I supervised the candidate and evaluated the final version of the manuscript.

Signed Date 16/10/15

Philip J. van Eyk
I supervised ~~the~~ candidate, aided in the interpretation of the data, and evaluated the final version of the manuscript.

Signed Date 16/10/15

Mikko Hupa
I supervised the candidate, aided in the design of experiments, and evaluated the final version of the manuscript.

Signed Date 19/10/2015

Rocky de Nys
I coordinated the cultivation of biomass for the experiments, aided in the interpretation of data, and evaluated the final version of the manuscript.

Date 22/10/15

David M. Lewis
I supervised the candidate, coordinated the cultivation of biomass for the experiments, and evaluated the final version of the manusc

Signed Date 27/10/15

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Algal Biomass: Occurrence of the Main Inorganic Elements and Simulation of Ash Interactions with Bed Material

Daniel J. Lane,*[,†] Maria Zevenhoven,[‡] Peter J. Ashman,[†] Philip J. van Eyk,[†] Mikko Hupa,[‡] Rocky de Nys,[§] and David M. Lewis[†]

[†]School of Chemical Engineering, University of Adelaide, Adelaide, South Australia 5005, Australia

[‡]Process Chemistry Centre, Åbo Akademi University, Piispankatu 8, 20500 Turku, Finland

[§]MACRO – the Centre for Macroalgal Resources and Biotechnology, and School of Marine & Tropical Biology, James Cook University, Townsville, Queensland 4811, Australia

ABSTRACT: The work presented here provides greater insight into the occurrence of the main inorganic elements in algae and how this varies for different species of algae and production methods. It also provides valuable insights into the behavior of algal ashes during combustion, particularly in regard to their interaction with quartz bed material, which is of direct relevance to agglomeration in fluidized bed reactors. A diverse range of algal species was selected for this work using a species of marine microalgae (*Tetraselmis* sp.) and marine macroalgae (*Derbesia tenuissima*) and a species of freshwater macroalgae (*Oedogonium* sp.). Two samples of *Oedogonium* were tested. One sample was cultivated using a standard nutrient addition regime, and the other was starved of essential nutrients at the completion of the culture cycle. Samples of algae were subject to chemical fractionation and the mode of occurrence of the main inorganic elements was inferred from their leaching behavior. Both the relative proportions of the main inorganic elements in the algae and their mode of occurrence are largely dependent on the culturing environment and harvesting history. The leaching behavior of the inorganic elements indicates a high level of inorganic, water-soluble, alkali salts in all of the tested algae. In order to simulate ash interactions with bed particles during fluidized bed combustion, pellets consisting of algal ashes mixed with quartz particles were heated in a muffle furnace at 850 °C in air. Scanning electron microscopy and energy dispersive spectroscopy analyses were performed on cross sections of the resultant samples. Melted ash coatings had formed on the surfaces of the quartz particles. In all cases there was no evidence of chemical reactions between the ashes and quartz particles. Melt-induced agglomeration appeared to be the principal agglomeration mechanism. The ashes from the two marine algae both formed salt-type melts. The ashes from the *Oedogonium* sample, which had been starved of essential nutrients during cultivation, formed a silicate-type melt. The resultant ash coating consisted of melted, Ca-rich, K–silicate. The *Oedogonium* sample grown under a standard nutrient addition regime had higher levels of P in its inorganic matter. The increased P content appeared to have a significant influence on the composition and adhesive behavior of the formed melt. The melt formed from the ashes of the P-rich *Oedogonium* sample had the greatest affinity for the quartz particles and the strongest tendency to form bridges. The resultant ash coating consisted of melted alkali silicate with discrete dispersions of alkali phosphate rich in Ca and Mg.

1. INTRODUCTION

Diminishing fossil fuel reserves and augmenting pressure to reduce greenhouse gas emissions has provided strong motivation to develop the utilization of biomass fuel technologies. Algal biomass is a promising feedstock with several key advantages over terrestrial biomass as an energy source. The production of algae has excellent potential for high energy yields per unit area of land with productivities as high as 70 dry tonnes ha^{-1} $year^{-1}$ commonly reported in the literature[1] for both macro- and microalgae species. Furthermore, algae can be produced in a broad range of aquatic environments including freshwater,[2] seawater,[3] and various types of wastewater.[4−6] Its cultivation does not require arable land, and the need for expensive nutrient inputs can potentially be circumvented by making use of nutrients available in eutrophic wastewaters.[7]

Combustion is one possible pathway for converting algal biomass to energy. The combustion behavior of several terrestrial biomass fuels is well understood, and many developed technologies already exist for converting these fuels. In contrast, the combustion behavior of algae is not well understood and, notably, the feedstock alternatives across the breadth of algae are extremely diverse. In our last paper,[8] we studied the behavior of nitrogen release and gasification reactivity of a range of algae types. This paper focuses on the characteristics of the inorganic matter from these algae, as major operational problems in biomass combustion systems are ash related.[9] These include fouling and high temperature corrosion, both of which are temperature sensitive.[10] Fluidized bed (FB) reactors operate at relatively low temperatures and are, therefore, an attractive technology for converting biomass fuels with problematic ash chemistry. However, bed agglomeration, which involves the sticking together of inert bed particles by ash compounds formed from inorganic components in the fuel, is prone to occur in FB combustion applications.[11] Bed agglomeration disrupts normal fluidization

Received: May 1, 2014
Revised: June 19, 2014
Published: June 23, 2014

ACS Publications © 2014 American Chemical Society

dx.doi.org/10.1021/ef500989n | *Energy Fuels* 2014, 28, 4622−4632

Table 1. Summary of the Algal Species Used in This Study

abbreviation	species	micro-/macroalgae	water	added nutrients
Tet	*Tetraselmis* sp.	micro	sea water	CO_2, $NaNO_3$, H_2PO_4
Deb	*Derbesia tenuissima*	macro	sea water	CO_2, f/2 medium[a]
OD + N	*Oedogonium* sp.	macro	fresh water	CO_2, MAF[b]
OD − N	*Oedogonium* sp.	macro	bore water	none

[a]A standard nutrient medium used to grow marine algae. [b]Microalgae Food. Both MAF and f/2 media contain nitrate, phosphate, and various trace metals.

behavior and, if severe enough, can lead to expensive reactor shut-downs. The proper characterization of the inorganic matter is, therefore, of utmost importance in the prediction and mitigation of ash-related problems during the combustion of algae. However, limited work has been undertaken to quantify the characteristics of inorganic matter in algae or understand its role in bed agglomeration.

The fate of the inorganic matter during combustion and its role in ash-related problems depends on the relative proportions of the main inorganic elements and their associations in the fuel.[12] The association of inorganic elements has been extensively studied in coal[13,14] and a diverse range of terrestrial biomass fuels.[15−18] The inorganic matter in coal is characterized by a high proportion of mineral matter, whereas the inorganic matter in biomass tends to contain more water-soluble salts and inorganic elements associated with organic components in the fuel matrix. A number of studies[19−22] have reported the concentrations of the inorganic elements in a range of algal species with the main inorganic elements as Si, Fe, Ca, Mg, P, Na, K, S, and Cl. The concentrations of these elements vary widely both within and between species and are largely dependent on the cultivation environment, particularly the availability of nutrients. However, studies are often only conducted at an elemental level and do not consider speciation. Furthermore, studies focused on the speciation of the inorganic elements in algae are rarely quantitative and tend to focus only on individual elements and on a narrow range of algal species. This has resulted in a knowledge gap that prevents the accurate prediction of the roles of the inorganic elements in algal biomass in ash-related problems such as bed agglomeration.

There has been a vast amount of research aimed at understanding bed agglomeration during fluidized bed combustion of both coal and terrestrial biomass. Skrifvars et al.[23] established three key mechanisms for ash sintering in coals: partial melting, viscous flow sintering, and gas−solid chemical reaction. Viscous flow sintering tends to be the principal mechanism for anthracite and bituminous coals,[23] whereas partial melting tends to be the principal mechanism for brown coals,[23] presumably because their ashes contain a higher proportion of compounds that melt at low temperatures. Partial melting of ashes leads to the formation of a sticky coating on the surface of char particles[24] that, when transferred to the surface of bed particles, acts as glue for agglomerate formation.[24] This process is known as melt-induced agglomeration and occurs with both coal and biomass fuels. Brus et al.[25] and de Geyter et al.[26] both provide excellent reviews on the principal agglomeration mechanisms in terrestrial biomass fuels with a low content of P. In addition to melt-induced agglomeration, coating-induced agglomeration involving the initial chemical attack of bed particles by gas or liquid phase alkali species is a key mechanism in many biomass fuels, particularly wood. More recent studies[27−30] have focused on P-rich biomass fuels. The agglomerating behavior of this category of fuels is still not fully understood. Phosphorus is capable of forming sticky alkali-phosphate melts of high viscosity,[31] which form preferentially over alkali silicates[27] (typically formed by Si-rich fuels). In fuels with a surplus of alkali metals, both alkali phosphates and alkali silicates can form;[27,29] however, the interactions between the two phases are not well understood. In many species of algae, P, Si, and alkali metal concentrations are all high. This makes the agglomerating behavior of algal fuels difficult to predict based on previous experience with terrestrial fuels alone, and literature regarding the agglomerating behavior of algal fuels is scarce. Clearly, more insights are needed for a proper understanding of the agglomerating behavior of algal biomass during FB combustion and to understand how the behavior varies for different algae types. Therefore, the first aim of this study was to better understand the occurrence, and in particular the speciation, of the main inorganic elements in a diverse range of algae species grown under different conditions. The second aim was to provide insight into the interactions that take place between algal ashes and bed material during FB combustion.

2. EXPERIMENTAL SECTION

2.1. Algal Species. A diverse range of algae was selected for this work. The selected species are summarized in Table 1. Samples include species of micro- and macroalgae as well as freshwater and marine algae. The species of *Oedogonium* used in this work is highly competitive in freshwater environments[2] and is noted for its use in bioremediation.[32] It is currently being considered for the treatment of wastewater derived from agriculture[7] and coal-fired power plants.[6] The species of *Tetraselmis* and *Derbesia* are both prospective feedstocks for commercial biofuel production.[33,34]

A broad range of culturing methods was used to produce the algae used in this work. Detailed descriptions of the growth and harvesting methods can be found elsewhere.[8,35] Only a brief summary is provided here. The *Tetraselmis* biomass (hereafter referred to as "Tet") was grown in an outdoor seawater pond. CO_2 and commercial grade nitrate and phosphate were added to the pond as nutrients. All other essential nutrients were sourced from the seawater medium. The *Derbesia* biomass (hereafter referred to as "Deb") was grown in a 2500L seawater tank. CO_2 and f/2 growth media were both added to the tank as nutrient sources. The f/2 media[36] is a standard nutrient mix that contains nitrate, phosphate, and various trace metals and is commonly used to grow marine algae. *Oedogonium* was grown using two different culturing strategies. One variant of *Oedogonium* (hereafter referred to as "OD − N") was cultured in bore water and was starved of essential nutrients during the final stages of cultivation. The other (hereafter referred to as "OD + N") was cultivated using a standard nutrient addition regime of CO_2 and MAF (microalgae food), a nutrient mix similar to f/2 media, in dechlorinated freshwater. The three macroalgae (OD + N, OD − N, and Deb) were harvested by filtration through mesh bags followed by centrifugation. The microalga (Tet) was harvested by electroflocculation followed by centrifugation. The harvested biomass samples were dried to a moisture content of less than 10 wt %. The microalga (Tet) formed clusters of various sizes when dried. The dried macroalgal biomass consisted of tufts of intertwined filaments. In order to reduce the algae to a common size,

dx.doi.org/10.1021/ef500989n | *Energy Fuels* 2014, 28, 4622−4632

Table 2. Proximate, Ultimate, and Heating Value Analyses of the Tested Algae[8]

	proximate analysis (wt %)				ultimate analysis (wt %)[e]					
algae	moisture[a]	VM[b,c]	FC[d,c]	Ash[c]	C	H	N	O	S	higher heating value (MJ/kg)[e]
Tet	7.9	41.9	<1.0	64.4	42.1	8.7	6.7	35.4	6.9	15.5
Deb	6.6	74.8	15.1	10.1	52.6	7.2	7.6	30.9	1.3	21.7
OD + N	6.2	77.3	14.7	8	49.1	6.8	4.5	39.2	0.12	19.4
OD − N	8.2	77.2	6.1	16.7	47.4	6.8	1.5	44.1	0.2	17.4

[a]After drying. [b]Volatile matter. [c]Dry basis. [d]Fixed carbon. [e]Dry and ash-free basis.

representative samples of each macroalga were milled using a centrifugal knife mill and then sieved to pass through a 1 mm screen. The microalgal sample was also sieved through a 1 mm screen to remove coarse clusters. Proximate, ultimate, and heating value analyses of the resultant samples of algae are presented in Table 2.

2.2. Chemical Fractionation Experiment. In our last paper[8] we measured the main inorganic elements in the same samples of algae used in this work (Tet, Deb, OD + N, and OD − N). The main inorganic elements were Si, Ca, Mg, P, Na, K, S, Cl, Fe, and Al. Chemical fractionation was used to characterize the leaching behavior of these elements. The chemical fractionation process is summarized in Figure 1. Samples (25g) of the milled algae were subject to consecutive leaching with increasingly aggressive solvents (H_2O, 1 M NH_4Ac, and 1 M HCl). The result was four fractions, three liquid fractions and one rest fraction that contained the insoluble residue. The concentrations of the main inorganic elements in the four fractions were determined according to modified EPA methods 200.7 and 200.8. The measurement systems used were inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inductively coupled plasma sector-field spectrometry (ICP-SFMS). The rest fraction was first digested using $LiBO_2$ and HNO_3. Sample digestions and elemental analyses were all performed externally by Belab AB and ALS Scandinavia (accredited laboratories in Sweden).

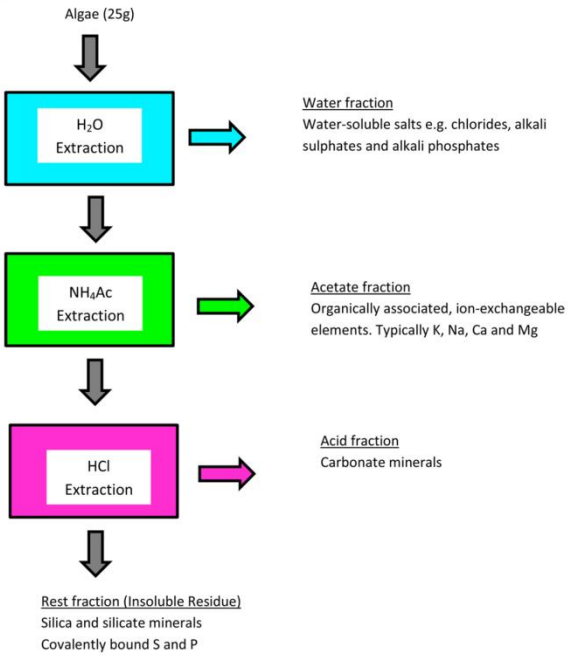

Figure 1. Schematic of the chemical fractionation process.

The distribution of the main inorganic elements among the four fractions shows which of the inorganic elements occur together in the algae and can be used to infer their mode of occurrence. The water fraction contains several simple salts such as alkali and alkaline earth metal chlorides, alkali sulfates and alkali phosphates. These salts precipitate in a water-soluble form when the alga is dried. The acetate (NH_4Ac) fraction contains organically associated inorganic elements that are present in ion exchangeable form (e.g., K or Ca connected to carboxylate groups). The acid (HCl) fraction contains precipitated carbonate minerals and the rest fraction silica (SiO_2) and various silicate minerals. It also contains S and P, which are covalently bound to organic components in the fuel matrix.

Chemical fractionation has been extensively employed to understand the association of the inorganic elements in both coal and terrestrial biomass. The leaching program used in this study was based on an in-house method developed for terrestrial biomass fuels at Åbo Akademi University in Turku, Finland. The in-house method[15] was modified in the following two ways to account for morphological differences between terrestrial biomass and algae. First, greater solvent to biomass ratio was used (25 g of solvent:1 g of biomass). A ratio of 5:1 is normally used for wood-derived fuels, and a ratio of 10:1 for agricultural residues. This was needed to achieve adequate wetting of the macroalgal samples that were highly porous. Second, ultrafine (2.7 μm) filter paper was used to filter the microalgae particles. When in solution, the dried microalgae aggregates breakdown and can potentially pass through more coarse filters.

2.3. Ash-Bed Material Interaction Experiment. In order to simulate ash interactions with bed particles in a FB reactor, pellets consisting of algal ashes mixed with quartz particles were heat treated in a muffle furnace. The resultant samples were then analyzed by means of scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The ashes were prepared at a mild temperature (550 °C) according to European Standard CEN/TS 14775 to limit the evaporation of volatile inorganic species and then stored in a desiccator. The dry ashes were thoroughly mixed with high purity quartz particles of size 212−355 μm to prepare ash/quartz mixtures containing 40 wt % ash and the balance quartz. The quartz particles had been heat treated at 1000 °C for 12 h to remove any organic contaminants. Aliquots 0.6−1.0 g in size of the ash/quartz mixtures were pressed into pellets of 10 mm diameter and 5−7 mm height using a hydraulic press and applying 200 bar compressive force in order to bring the ashes into close contact with the quartz particles. The pellets were then heated to 850 °C in a muffle furnace at a rate of 10 °C/min and then held at temperature for 6 h. After cooling to room temperature, the heat treated pellets were coated in an epoxy resin and then dry-ground and polished using silicon carbide paper to expose a cross section. Representative areas within the pellet cross sections were selected and SEM images recorded at two magnifications (100× and 500×). A backscatter electron detector (BSE) was used to reveal differences in chemical composition. SEM images recorded at 100× magnification include at least 10 quartz particles and show the interactions between the algal ashes and quartz particles. EDS area analyses were performed on multiple areas within the ash coatings to determine the bulk elemental composition of the ash coatings. SEM images recorded at 500× magnification include only 1 or 2 quartz particles and show more clearly differences in chemical composition within the ash coatings. EDS point analyses were performed on regions of different chemical composition within the ash coatings to determine the spatial distribution of the main inorganic elements.

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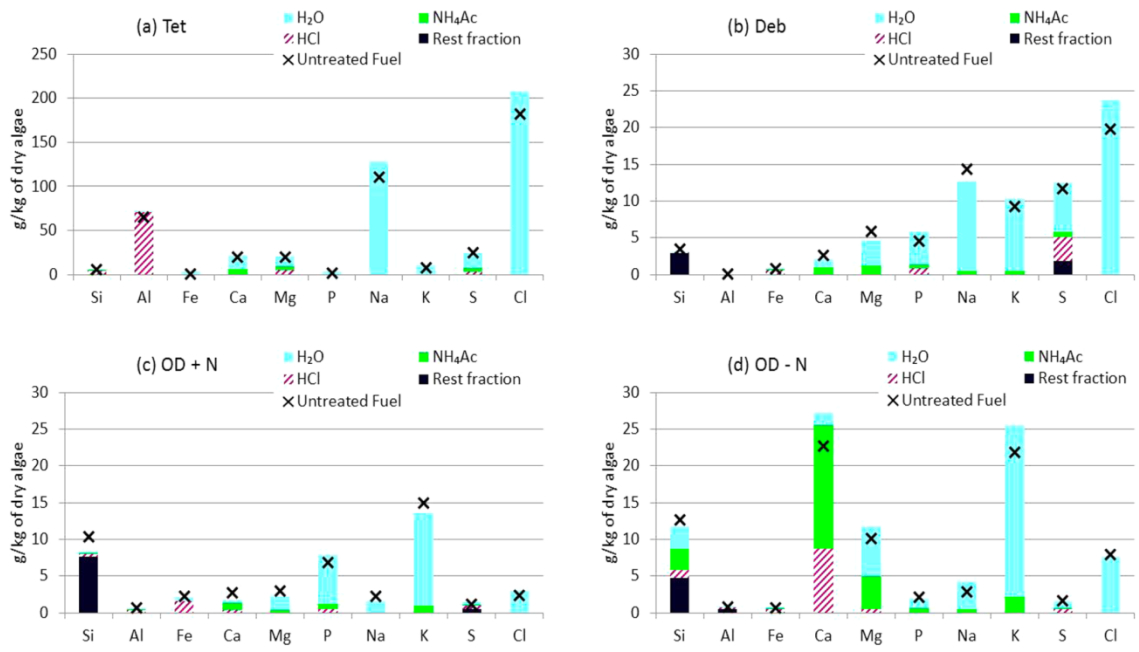

Figure 2. Chemical fractionation results for (a) *Tetraselmis* (Tet), (b) *Derbesia* (Deb), (c) *Oedogonium* grown under a standard nutrient addition regime (OD + N), and (d) *Oedogonium* starved of essential nutrients during cultivation (OD − N). The scale on the *y* axis for Tet is higher to account for the greater ash content of Tet.

3. RESULTS AND DISCUSSION

3.1. Occurrence of the Main Inorganic Elements. The results from the chemical fractionation experiment are presented in Figure 2. Concentrations of the main inorganic elements in the untreated algae were measured in addition to their concentrations in the four fractions (H_2O, NH_4Ac, HCl, and rest) to check the mass balance closures. The crosses in Figure 2 show the concentrations of the inorganic elements in the untreated algae and the bars show the concentrations in the four fractions. All concentrations are expressed as grams per kilogram of dry algae. In most cases, the sum of the four fractions are within about 25% of the value of the untreated algae. The *y*-axis scale on the plot for Tet is an order of magnitude greater than that for the three macroalgae (Deb, OD + N, and OD − N). This is to account for the extremely high ash content of Tet (64%). The substantial amount of ash in Tet is attributed to the saline growth medium and to the electroflocculation process used to harvest the algae. The electroflocculation process involves the application of a current to sacrificial aluminum electrodes, which provides cations for flocculation.[8] Not only is microalgae flocculated in this process but foreign matter in the pond is also included. Extracellular material is further concentrated in the biomass by evaporating off residual moisture from the harvested biomass.

The relative proportions of the main inorganic elements in the algae and their distributions over the four different fractions are shown clearly in Figure 2. In terms of relative proportions, the main inorganic elements in the two marine algae (Tet and Deb) are Cl and Na. These two elements constitute approximately one-third of Tet by weight on a dry basis (d.b.). Tet also contains a substantial amount of Al (6.5 wt % d.b.) that primarily originates from the aluminum electrodes used in the electroflocculation process. Concentrations of Na and Cl are an order of magnitude lower in Deb. This is a direct result of rinsing Deb in freshwater immediately after harvesting. Deb also contains much higher proportions of K, S, P, Mg, and Ca in its inorganic matter than does Tet. The relative proportions of the main inorganic elements in the two samples of the freshwater macroalga *Oedogonium* (OD + N and OD − N) are significantly different to their proportions in the marine algae. Potassium is the main alkali metal in *Oedogonium* rather than Na. This is generally the case in terrestrial plants;[37] however, in several brown coals[38] Na concentrations can outweigh K concentrations. The concentration of Cl in OD + N is an order of magnitude lower than in Deb, 2 orders of magnitude lower than in Tet, and is similar to that in rapeseed cake.[18] The concentration of Cl in OD − N is approximately twice the concentration in OD + N; however, it is still lower than the concentration in the marine algae. The bore water used to cultivate OD − N is presumably responsible for the higher Cl content in OD − N. Sulfur concentrations are also lower in the freshwater algae. This result was expected given that the concentration of sulfate ions is normally higher in marine waters than in freshwaters.[39] There are also significant differences in the proportions of the main inorganic elements in the two *Oedogonium* samples (OD + N and OD − N) which indicate that the composition of *Oedogonium* is largely dependent on the composition of the growth medium. The main inorganic elements in OD + N are K, Si, and P. In OD − N, K, Ca, Si, and to a lesser extent Mg are the main inorganic elements. The higher alkaline earth metal content in OD − N is a result of OD − N being cultivated in bore water rich in carbonates. OD − N is also comparatively lower in both P and Fe. This is a direct result of OD − N being starved of these two nutrients during cultivation.

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3.1.1. Chlorine. Chlorine in the two marine algae (Tet and Deb) originates from seawater and in OD − N originates from bore water. In the case of OD + N, Cl originates from the MAF nutrient mix which contains Cl in the form of various metal chlorides. Chlorine is more or less completely water-soluble in all of the tested algae and almost certainly exists as precipitated alkali metal chlorides. In terrestrial plants, Cl is usually water-soluble unless the biomass has been contaminated with poly(vinyl chloride).[15]

3.1.2. Sodium and Potassium. The alkali metals in algae are usually highly mobile and play a role in osmoregulation.[40,41] Virtually all of the Na and over 90% of the K in the tested algae are water-soluble. The molar ratios of Cl to water-soluble Na and K in the tested algae are presented in Figure 3 and are

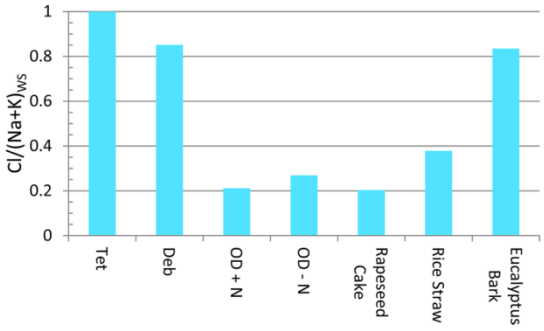

Figure 3. Molar ratios of chlorine to water-soluble (WS) alkali metals (Na + K) in the tested algae (Tet, Deb, OD + N, OD − N). Data for the algae are compared to chemical fractionation data reported in the literature for terrestrial biomass by Piotrowska et al.[18] (rapeseed cake) and by Skrifvars et al.[42] (rice straw and eucalyptus bark).

compared to the ratios reported in the literature for rapeseed cake,[18] rice straw,[42] and eucalyptus bark.[42] The chloride-to-alkali ratio is commonly used to indicate the proportion of the alkali metals present as chloride salts. The alkali metals in Tet likely exist almost exclusively as chloride salts. In Deb, approximately three-quarters of the water-soluble alkali metals are expected to exist as chloride salts, which is similar to the occurrence of the alkali metals in eucalyptus bark. The balance is mainly associated with the water-soluble fractions of S and P in the form of inorganic sulfates and phosphates. As expected the chlorine to alkali metal ratios in the two freshwater algae are significantly lower (20% in OD + N and 28% in OD − N, respectively). The ratio in OD + N is similar to that in rapeseed cake. The vast majority of the remaining water-soluble Na and K in OD + N are probably connected with the water fraction of P in the form of inorganic phosphate salts. In OD − N, alkali carbonates are expected to account for much of the balance. A small amount of the total K (approximately 10%) in the macroalgae (Deb, OD + N, and OD − N) is found in the acetate fraction. Potassium found in this fraction probably occurred as a counterion to organic anions in the algae such as carboxylate groups.

3.1.3. Calcium and Magnesium. The distribution of Ca over the four fractions varies substantially for the different algae indicating major differences in its mode of occurrence. The majority of Ca in the two marine algae (Tet and Deb) is water-soluble whereas the majority of Ca in the two freshwater algae (OD − N and OD + N) is found in the acetate fraction. Water-soluble Ca was most likely associated with inorganic anions, especially nitrate. Acetate−Ca is expected to have occurred mainly as a counterion to carboxylate groups of complex polysaccharides. A significant amount of Ca is also found in the acid fraction of OD + N (18%) and OD − N (32%). It is expected that this Ca occurred as precipitated calcite (calcium carbonate), which is usually the main mineral deposit found in freshwater algae.[43] This is in contrast to wood where typically a large amount of Ca is stored in the form of oxalate minerals.[16] Most of the Mg present in the algal samples is water-soluble. The balance is found predominantly in the acetate fraction for the three macroalgae (Deb, OD + N, and OD − N) and in the acid fraction for Tet. Water-soluble Mg is most likely present as nitrate salt. Magnesium sulfate may also account for a portion of the water-soluble Mg in the two marine algae (Tet and Deb). Acetate−Mg is likely present in similar forms to acetate−Ca. Acid−Mg in Tet was presumably precipitated from the growth medium during electroflocculation in the form of extracellular magnesium hydroxide.

3.1.4. Phosphorus. Phosphorus is an essential macronutrient for algal growth and for cellular processes such as energy transfer and nucleic acid synthesis.[44] The majority (67−84%) of the P in the macroalgae (Deb, OD + N and OD − N) is water-soluble. It is well known that algae are capable of storing significant amounts of inorganic phosphate in discrete aggregates.[45] These aggregates, which are typically rich in K,[46] are expected to be the principal form of P occurrence in the macroalgae. The principal form of P storage is different in agricultural crops where P is normally stored in the form of phytic acid and its salts, phytates.[47] Phosphorus in algae also occurs in metabolic forms,[40,41] such as phospholipids and nucleic acids. Such forms probably account for the P found in the acetate and acid fractions of the macroalgae. Phosphorus in Tet is almost exclusively acid soluble and is almost certainly connected with acid-soluble Al in the form of extracellular aluminophosphates. Phosphate present in the growth medium reacts readily with Al cations,[48] which are released in vast quantities during the electroflocculation process.

3.1.5. Sulfur. Sulfur is required by algae for the synthesis of specific lipids and two key amino acids: cysteine and methionine.[49] It is generally taken up from the growth medium in the form of sulfate ions and when present in excess is stored as inorganic sulfate in cell vacuoles.[41] Most of the S in Tet, Deb, and OD − N is water-soluble and presumably occurs as inorganic sulfates. The association of S in straw is similar. Between 40 and 80% of the total S in straw is water-soluble[50,51] and occurs mainly as inorganic sulfate.[51] In wood, on the other hand, three-quarters of the total S is associated with organics.[16] In OD + N and Deb, a significant proportion of the total S is found in the acid and rest fraction. It is suspected but not confirmed that a large part of the acid−S was present as precipitated FeS from the growth media given that Fe was also found in the acid fraction of Deb and OD + N. Sulfate reducing bacteria reduce sulfate to H_2S which readily combines with Fe to precipitate FeS.[52] Insoluble S is probably covalently bound to organic components in the fuel matrix.[15]

3.1.6. Silicon. Silicon is a key structural constituent of algal cell walls.[41,53] It is taken up from the growth medium in the form of orthosilicic acid (H_4SiO_4) and is transported to cell walls where it polymerizes and precipitates as silica, normally in amorphous form.[54] The vast majority of Si in Tet, Deb, and OD + N is insoluble and presumably exists as precipitated amorphous silica. Silicon solubility in most terrestrial plants[15] is also low except in some fast-growing plants such as straw,

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where as much as 25% of the total Si can occur in a water-soluble form.[55] The leaching behavior of Si in OD − N differs remarkably from that in the other samples of algae. Approximately half of the Si in OD − N is found in the water and acetate fraction. It is suspected that the higher solubility of Si in OD − N is due to it being cultivated in a growth medium with a higher pH than the growth media used to cultivate Tet, Deb, and OD + N. Amorphous silica is only marginally soluble in water with pH values below about 8.5; however, above this value, its solubility increases rapidly.[56] In the case of Tet, Deb, and OD + N, CO_2 was added to the growth media as a nutrient which has the effect of decreasing pH. The pH of the growth media used to culture these samples was kept below 8.5 during the day. Conversely, no CO_2 was added to the growth medium used to culture OD − N and, as a consequence, it had a much higher pH (estimated to be around 9.5−10 at the time of harvesting).

3.1.7. Aluminum. The Tet sample contains a substantial amount of Al that is found almost exclusively in the acid fraction. Aluminum in Tet originates from the electrodes used in the electroflocculation process and is expected to occur mainly in the form of aluminum hydroxide but also in the form of metallic fragments that had detached from the electrodes. A small amount of Al (<0.1 wt %) is found in the acid and insoluble fractions of the two *Oedogonium* variants. This indicates the presence of a small amount of aluminosilicates (clay contaminants). Virtually no Al was detected in the Deb sample.

3.1.8. Iron. Iron is a key component of several proteins in algae and is involved in many functions related to cellular metabolism.[57] In Deb, Tet, and OD − N, Fe is present in negligible proportions and is unlikely to significantly influence their ash chemistry. Only in OD + N is Fe present in significant proportions. In OD + N, Fe is found mainly in the acid fraction (75%) but also in the water fraction (25%). Iron is fed to OD + N with a chelating agent (EDTA) to prevent its precipitation so that it can be assimilated by the alga. When released from the chelating agent, Fe is readily precipitated from the growth medium.[44] Precipitated Fe, especially in the form of FeS,[52] is expected to account for a large part of the Fe found in the acid fraction. Water-soluble Fe may simply be in the form of residual nutrient (still attached to the chelating agent) or may be organically associated, particularly with protenacious bodies[45] that have been reported[41] to be at least partially water-soluble.

3.2. Ash-Bed Material Interactions. In order to better understand the interactions that take place between algal ashes and bed material in a FB reactor, ash-bed interactions were simulated by heat treating (850 °C) pellets consisting of algal ashes mixed with quartz particles. Cross sections of the resultant samples were then analyzed by means of SEM/EDS. Figure 4 shows micrographs of algal ash interactions with quartz particles taken using a BSE detector. The darker particles in Figure 4 are the quartz grains and the lighter material the ash-rich coatings. The cracks in the quartz grains were formed as a result of compression of the ash/quartz mixtures during pelletization. It is clear that the ash coatings were at least partially molten at 850 °C. The ashes from the different algae interacted with the quartz grains to various extents. The ashes from OD + N had the greatest tendency to form bridges between quartz particles and penetrated deep into the cracks in the quartz grains. The ashes from Tet showed the weakest interaction with the quartz particles. Interestingly, the majority of the quartz particles are not even in contact with the ash from

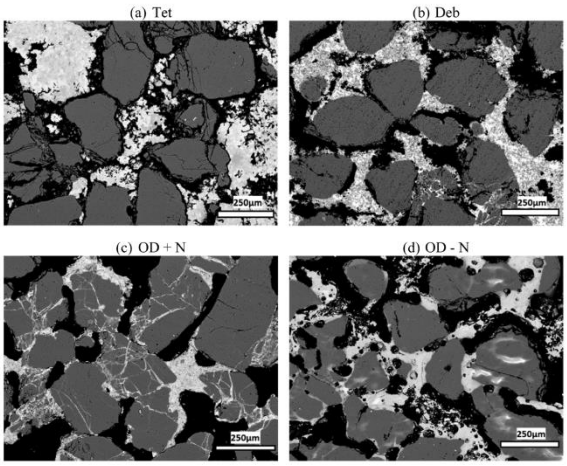

Figure 4. Micrographs of algal ash interactions with quartz grains for (a) Tet, (b) Deb, (c) OD − N, and (d) OD + N. The darker particles are the quartz grains and the lighter material the ash coatings.

Tet. Presumably, the ashes were in contact with the quartz particles at 850 °C but became detached due to thermal stress upon cooling the ash/quartz pellets.

3.2.1. Ash Coating Composition. The bulk elemental compositions of the ash coatings in Figure 4 were determined by taking EDS area analyses of 10 different regions in the coatings. The results are presented on a carbon-free basis in Figure 5. The coatings from the two marine algae (Tet and

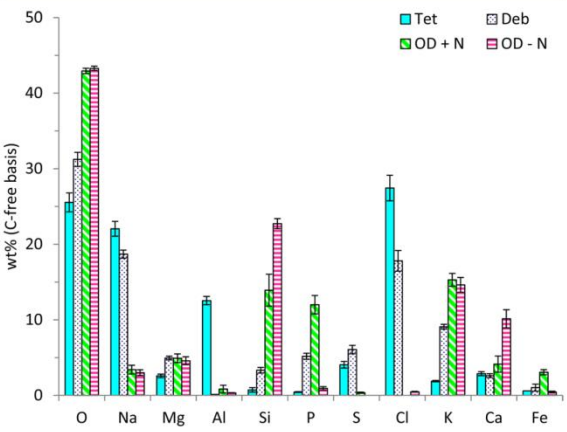

Figure 5. Bulk elemental compositions of the ash coatings shown in Figure 4. Error bars represent ±1 standard deviation.

Deb) contain substantial amounts of Na and Cl (35−49 wt % on a C-free basis), which indicates the presence of unreacted NaCl in the coatings given the high initial levels of NaCl in the algae. Chlorine, in the form of alkali chlorides, is highly volatile under typical combustion conditions[58] and is rarely found in significant concentrations in bed agglomerates from terrestrial fuel combustion. The mechanism of Cl release has been extensively studied in terrestrial fuels[58−60] and involves two steps. The first step involves the reaction of alkali chlorides with proton donor sites in the fuel matrix and the release of Cl as HCl. The second step involves the evaporation of alkali

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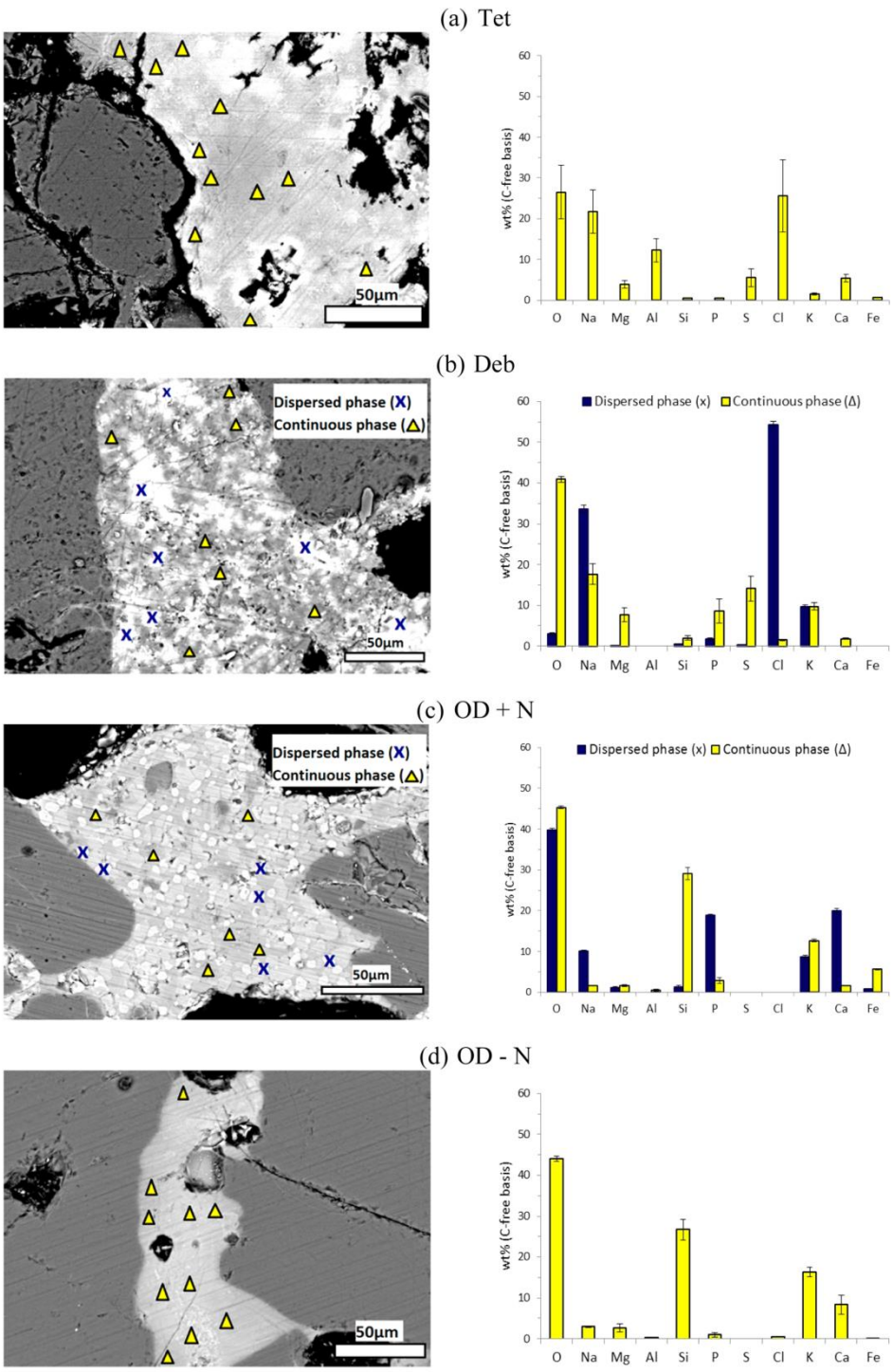

Figure 6. Left: Close-up SEM images of ash coatings for (a) Tet, (b) Deb, (c) OD − N, and (d) OD + N. The images were taken using a BSE detector to reveal differences in chemical composition within the ash coatings. EDS point analyses were performed at regions within the ash coating of different chemical composition in order to determine the spatial distribution of the main inorganic elements. Two separate ash phases were identified in the ash coatings from Deb and OD + N. Error bars represent ±1 standard deviation.

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chlorides. Step 1 occurs below 500 °C and is the principal release mechanism for low-Cl fuels such as wood.[58] Chlorine release during Step 1 is limited by the number of proton donor sites available for alkali capture and the remaining Cl is released by Step 2, between 700−850 °C. Step 2, tends to be the main release mechanism for fuels with high Cl contents such as straw.[58] Given the fact that virtually all of the Cl in the marine algae occurs as alkali chlorides, it was expected that all of the Cl would have been released by Step 2. It is suspected, but not confirmed, that mass transfer limitations caused by the dense packing of the ash and quartz particles in the pellets prevented the complete release of Cl. Unlike Cl, Na is often found in high concentrations in ash coatings from terrestrial fuels; however, it is usually associated with sulfates, phosphates, or silicates. The ash coating from Tet also contains a substantial level of Al (13 wt % on a C-free basis), most likely in the form of alumina (Al_2O_3).[15] The ash coating from Deb contains significant amounts of K, S, P, Mg, and Ca in addition to Na and Cl. Of these elements, Mg is relatively inert[15] at the temperature used in this study (850 °C) and is expected to have been mainly retained in the ash coating. Mg was used to trace the release of more volatile inorganic elements in Deb by comparing its concentration in the original fuel sample (see Figure 2) to its concentration in the ash coating (see Figure 5). The [S]:[Mg] ratio in the ash coating from Deb is about 40% lower than that measured in the fuel. This indicates that S is preferentially released to the gas phase during combustion. This finding is consistent with experiments by Knudsen et al.[58] on the release of S from agricultural crops. Knudsen et al.[58] reported that 40−70% of the S in agricultural crops is released to the gas phase by 850 °C.

The main inorganic elements in the ash coatings from the freshwater algae (OD + N and OD − N) are Si, K, Ca, and Mg. Phosphorus is present in high concentrations in the ash coating from OD + N (12 wt % on a C-free basis) but not in the ash coating from OD − N (<1 wt % on a C-free basis). This was expected based on the chemical fractionation results (Figure 2), which show OD + N to have much greater proportions of P in its inorganic matter than OD − N. There are some key differences in the compositions of the ash coatings from the freshwater algae when compared to the ash coatings from the marine algae. Chlorine levels in the ash coatings from the freshwater algae are negligible which is consistent with the trend in terrestrial fuels. Sulfur levels are also negligible. This was expected given the low content of S in these two algae. Silicon levels are much greater (up to an order of magnitude) in the coatings from the freshwater algae and K levels outweigh Na levels (4−5 times). These differences all largely reflect the initial compositional differences in the inorganic matter of the marine and freshwater algae.

Close-up micrographs of regions within the ash coatings were taken to gain insights into the spatial distribution of the main inorganic elements. Such insights help in understanding what phases are present in the ash coatings. The micrographs and corresponding EDS analyses are presented in Figure 6 for each of the tested algae. The ash coating from Tet clearly consists of melted NaCl given the extremely high concentrations of Na and Cl (47 wt % on a C-free basis) in the coating. Other inorganic elements, including Al, appear to be dissolved in the melted salt. Ash coatings consisting primarily of NaCl are uncommon in terrestrial fuel combustion since fuels with Cl contents greater than about 1 wt % are rarely studied.

The ash coating from Deb is clearly heterogeneous in composition and consists of two separate salt phases. The interface between the two phases is not well defined. The continuous phase contains mainly Na and Cl (88 wt % on a C-free basis), presumably in the form of melted NaCl. The dispersed phase is enriched in P, S, Ca, and Mg and most likely consists of an alkali and alkaline earth metal phosphate/sulfate mixture. Potassium is uniformly distributed throughout the coating.

The ash coating from OD − N is more or less homogeneous in composition. It presumably consists of melted, Ca-rich, K−silicate given that Si, K, and Ca are the three main elements in the coating and that a substantial amount of the Si in OD − N is found in the water and acetate fraction during chemical fractionation. Soluble Si is usually reactive[55] and results in almost complete formation of low-temperature melting alkali silicates.[11] In the case of fuels with high levels of reactive Si such as wheat straw, silicate coatings on bed particles are formed by the reaction of K with fuel-derived Si. It is expected that the ash coating from OD − N was formed by this mechanism. The mechanism is different than that which takes place during the combustion of fuels with low levels of reactive Si such as woody biomass. In the case of such fuels gaseous or aerosol phase K reacts with bed particle Si instead of fuel-derived Si. This reaction is generally accompanied by diffusion of Ca into the silicate melt resulting in the formation of two distinct layers; an inner layer consisting of Ca−K−silicate and an outer layer with a composition that more closely resembles that of the ash. In the ash coating from OD − N, there are no signs of enrichment of any of the main inorganic elements at the quartz grain boundary or any other evidence to indicate chemical reactions between the ashes and quartz grains.

The ash coating from OD + N consists of a Si-rich continuous phase with discrete, globular-shaped, P-rich inclusions that are approximately 2−5 μm in diameter. The continuous phase is most likely melted silicate and the P-rich inclusions, phosphate. Silicates and phosphates have been found to segregate in a similar manner in the sintered ashes from wheat straw.[61] Interestingly, the vast majority of both Na (86%) and Ca (92%) in the ash coating from OD + N are found in the phosphate inclusions. Potassium, on the other hand, is uniformly distributed throughout the coating. Iron is concentrated in the silicate phase. Investigations into the agglomerating behavior of terrestrial biomass fuels[62] have shown the base cations (K, Na, Ca, Mg) to have a greater affinity for P than Si. This explains why Na and Ca are concentrated in the phosphate inclusions; however, it is unclear why K is concentrated in the silicate phase and not in the phosphate inclusions. In order to gain further insight into the segregation of the main inorganic elements in the ash coating of OD + N a small sample of OD + N was oxidized at a relatively low temperature (700 °C) and for a relatively short period of time (15 min). The gently prepared ash was then analyzed by means of SEM/EDS. The results from the analysis are presented in Figure 7. The combustion residues consist of two types of particles: (1) highly porous, spongelike particles and (2) smooth, well-defined blocks approximately 20−30 μm in length. Several EDS point analyses were performed on both particle types. The spongelike particles are concentrated in P and the block-shaped particles in Si. It is highly likely that P and Si occurred separately in OD + N, given the fact that these two elements were found in separate fractions in the chemical fractionation experiment. Sodium, Ca, and Fe are distributed

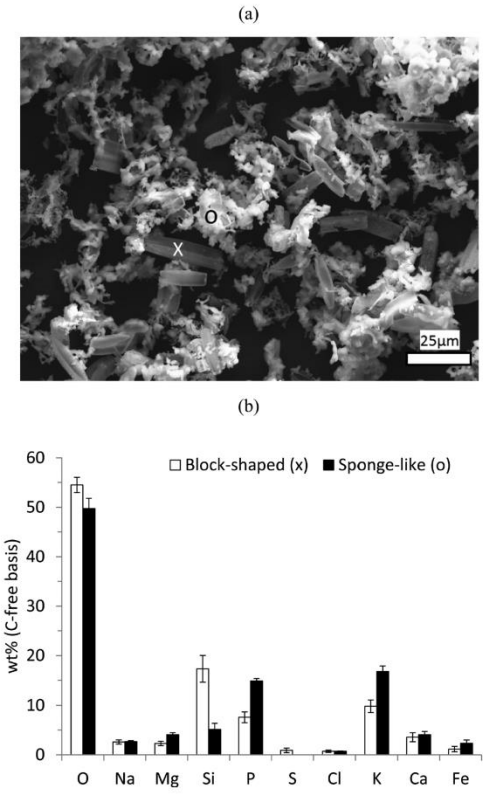

Figure 7. (a): Micrograph of OD + N combustion (700 °C) residues. Two different types of particles were identified in the residues: (1) spongelike particles and (2) block-shaped particles. A cross (×) is used to show an example of a spongelike particle and a circle (○) to show an example of a block-shaped particle. (b): Average elemental compositions of the spongelike particles and block-shaped particles. Several EDS point analyses of both types of particles were performed to calculate the average compositions. Error bars represent ±1 standard deviation.

fairly evenly between Particle Type (1) and Particle Type (2), which indicates that these elements had not yet started to segregate at 700 °C. It is possible that Na and Ca transfer from Particle Type (2) to Particle Type (1) and Fe from Particle Type (1) to Particle Type (2) between 700 and 850 °C. It is likely that the formation of molten ash above 700 °C facilitates this transfer.

3.2.2. Implications for Fluidized Bed Combustion. The formation of large amounts of low-temperature melting compounds in the ashes of algal biomass can be expected during FB combustion. Melt-induced agglomeration involving the sticking together of bed particles by an ash-derived melt appears to be the principal agglomeration mechanism for all of the tested algae. The inorganic matter in the marine algae (Tet and Deb) is characterized by high levels of water-soluble alkali salts that melt at temperatures typical of FB combustion. The formation of salt-type melts is the principal cause of agglomeration during FB combustion of Na and S rich South Australian Brown Coals.[24,63] The melt fraction controls the adhesiveness of the ash[64] and, therefore, influences the propensity for bed agglomeration. The inorganic matter in coal contains relatively high proportions of high-temperature melting minerals[14] that dilutes the concentration of melt in the ashes and, therefore, limits the stickiness of the ashes. The inorganic matter in marine algae on the other hand consists primarily of simple alkali salts (chlorides, sulfates, and phosphates) that melt at low temperatures and result in high melt fractions. The problem of a high melt fraction is compounded by high ash contents in the marine algae (10 wt % d.b. for Deb and 64 wt % d.b. for Tet). Severe bed agglomeration can therefore be expected during FB combustion of the marine algae.

In the case of the freshwater alga, OD − N, agglomeration is expected to be initiated by the formation of a silicate-type melt. The mechanism of melt formation is expected to be similar to that encountered during FB combustion of wheat straw,[27] which like OD − N contains a high level of reactive Si. The mechanism involves the reaction between K and fuel-derived Si to form low-temperature melting K−silicates. In the case of OD − N, a significant amount of Ca is included in the melt. The addition of inorganic phosphate to the growth medium used to culture OD + N means that P is present in much higher proportions in the inorganic matter of OD + N than in the inorganic matter of OD − N. The increased P content appears to have a significant influence on the composition and adhesiveness of the formed melt. The melt formed from the ashes of OD + N consists of both alkali silicates as well as alkali phosphates rich in Ca and Mg. The combined salt and silicate melt can be expected to be more aggressive than the silicate melt formed from the ashes of OD − N. The problem of bed agglomeration during FB combustion could potentially be alleviated by reducing the proportion of water-soluble alkali salts in both marine and freshwater algae. This could be achieved by deep washing of algal feedstocks in freshwater or by cofiring with a fuel rich in mineral matter such as coal.

■ CONCLUSIONS

The quantities of the main inorganic elements in two marine species (*Tetraselmis* sp. and *Derbesia tenuissima*) of algae and in two variants of a freshwater species (*Oedogonium* sp.) of algae have been determined and their associations in the biomass inferred from their leaching behavior. Both the relative proportions and the associations of the main inorganic elements are largely dependent on the cultivation environment and harvesting history. The inorganic matter of all of the tested algae is characterized by a high proportion of water-soluble alkali salts. Sodium is the main alkali metal in marine algae and exists mainly as chloride salts. In the freshwater species, *Oedogonium*, K is the main alkali metal. When *Oedogonium* is grown under a standard nutrient addition regime, K occurs mainly in the form of phosphate salts, whereas when *Oedogonium* is starved of essential nutrients, K exists as several salts.

Analysis of algal ash interactions with quartz particles showed melted ash coatings on the surface of the quartz particles. There were no clear signs of enrichment of any of the main inorganic elements at the interface between the ash coatings and quartz particles or any other evidence to suggest chemical reactions between the quartz particles and ashes for any of the algae. Melt-induced agglomeration, involving the sticking together of bed particles by an ash-derived melt, appeared to be the principal agglomeration mechanism. The composition of the formed melt and the extent to which the ashes interacted with the quartz particles varied significantly for the different species of algae and different culturing conditions. The ashes from the

sample of *Oedogonium* that had been starved of essential nutrients during cultivation formed a silicate-type melt. The resultant ash coating was more or less homogeneous in composition and consisted mainly of melted Ca-rich K−silicate. *Oedogonium*, when grown under a standard nutrient addition regime, contains much greater proportions of P in its inorganic matter. The increased P content appeared to have a significant influence on both the composition and adhesive behavior of the formed melt. The melt formed from the ashes of the sample of *Oedogonium* grown under a standard nutrient addition regime had the greatest affinity for the quartz particles and the strongest tendency to form bridges. The resultant ash coating consisted of a heterogeneous mixture of melted alkali silicate with discrete dispersions of alkali metal phosphates rich in Ca and Mg. The ashes from the marine algae both formed salt-type melts. The ash coating from Deb consisted of melted alkali metal chlorides and alkali and alkaline earth metal sulfates and phosphates. The ash coating from Tet consisted primarily of melted NaCl and remained only weakly attached to the quartz particles.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: daniel.lane@adelaide.edu.au.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The experimental work was carried out at the Process Chemistry Centre of Åbo Akademi University, Finland, within FUSEC (2011-2014), a project financed by the National Technology Agency of Finland (TEKES) and industrial partners Andritz Oy, Metso Power Oy, Foster Wheeler Energia Oy, UPM-Kymmene Oyj, Clyde Bergemann GmbH, International Paper Inc., and Top Analytica Oy Ab. Luis Bezerra and Linus Silvander are acknowledged for their technical support in various aspects of this work. This research was supported under Australian Research Council's Linkage Projects funding scheme (project number LP100200616) with our industry partner SQC Pty. Ltd. The project was also supported by the Australian Government through the Australian Renewable Energy Agency (ARENA) and the Advanced Manufacturing Cooperative Research Centre (AMCRC), funded through the Australian Government's Cooperative Research Centre Scheme. Andrew Cole and Marie Magnusson are acknowledged for their support in the production of macroalgal biomass. The authors also wish to acknowledge the support of Muradel Pty Ltd. and MBD Energy.

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Chapter 5

Paper III

Release of Cl, S, P, K, and Na during Thermal Conversion of Algal Biomass

Daniel J. Lane[a], Philip J. van Eyk[a], Peter J. Ashman[a], Chi W. Kwong[a], Rocky de Nys[b], David A. Roberts[b], Andrew J. Cole[b], and David M. Lewis[a]

[a]School of Chemical Engineering, The University of Adelaide, Adelaide, South Australia 5005, Australia

[b]MACRO – the Centre for Macroalgal Resources and Biotechnology, and School of Marine and Tropical Biology, James Cook University, Townsville, Queensland 4811, Australia

Energy & Fuels **2015**, 29 (4), pp. 2542 – 2554.

Statement of Authorship

Publication details: Lane DJ, van Eyk PJ, Ashman PJ, Kwong CW, de Nys R, Roberts DA, Cole AJ, Lewis DM. Release of Cl, S, P, K, and Na during thermal conversion of algal biomass. Energy & Fuels 2015; 29 (4): 2542-2554.

Publication status: Published

Author contributions:

By signing the Statement of Authorship, each author certifies that their stated contribution to the publication is accurate and that permission is granted for the publication to be included in the candidate's thesis.

Daniel J. Lane (Candidate)
Under the supervision of P. J. Ashman, P. J. van Eyk, and D. M. Lewis, I designed and performed the experiments, interpreted and processed the data, and wrote the manuscript.

Signed ..... Date 16/10/2015

Philip J. van Eyk
I supervised the development of work, aided in the development of the experimental method, aided in the interpretation of the data, and evaluated the final version of the manuscript.

Signed ..... Date 16/10/15

Peter J. Ashman
I supervised the candidate and evaluated the final version of the manuscript.

Signed ..... Date 16/10/15

Chi W. Kwong
I aided the candidate in the development of the experimental method and evaluated the final version of the manuscript.

Signed ..... Date 16/10/2015

Rocky de Nys
I coordinated the cultivation of biomass for the experiments and evaluated the final version of the manuscript.

Signed ..... Date 22.10.15

David A. Roberts
I cultivated biomass for the experiments and evaluated the final version of the manuscript.

Signed ..... Date 22/10/15

Andrew J. Cole
I cultivated biomass for use in the experiments and evaluated the final version of the manuscript.

Signed ..... Date 22/10/15

David M. Lewis
I supervised the candidate, coordinated the cultivation of biomass for the experiments, and evaluated the final version of the manuscript.

Signed ..... Date 27/10/15

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Release of Cl, S, P, K, and Na during Thermal Conversion of Algal Biomass

Daniel J. Lane,*[,†] Philip J. van Eyk,[†] Peter J. Ashman,[†] Chi W. Kwong,[†] Rocky de Nys,[‡] David A. Roberts,[‡] Andrew J. Cole,[‡] and David M. Lewis[†]

[†]School of Chemical Engineering, The University of Adelaide, Adelaide SA 5005, Australia

[‡]MACRO − The Centre for Macroalgal Resources and Biotechnology, College of Marine and Environmental Sciences, James Cook University, Townsville Qld 4811, Australia

ABSTRACT: The release of volatile inorganic elements during thermal conversion of algal biomass may cause operational problems in industrial reactors such as fouling, deposition, corrosion, and bed agglomeration. The release of Cl, S, P, K, and Na during the thermal conversion of algal biomass has been experimentally investigated in this paper. A freshwater macroalga (*Oedogonium* sp.), a freshwater polyculture of microalgae, and a marine microalga (*Tetraselmis* sp.) were used as feedstocks to assess the influence of different species and culturing environments on the release of the inorganic elements. Char and ash samples were prepared in a laboratory-scale fixed-bed reactor under isothermal conditions ranging from 500 to 1100 °C, under pyrolysis, combustion, and gasification atmospheres. The release of the inorganic elements was quantified by mass balances based on elemental analyses of the char and ash residues. Differences in the release of Cl, S, K, and Na were significant between the marine alga and the freshwater algae but were only minor between the freshwater microalgae and the freshwater macroalga. In the freshwater algae, the majority of the total Cl was released at low temperatures, below 500 °C. The majority of the fuel-S was also released at low temperatures. The remaining S was released with increasing temperature during combustion and gasification but was partially retained in the char during pyrolysis. Retentions of K and Na in the char and ash residues were both relatively high. Only 20−35% of the total K and 35−50% of the total Na in the freshwater algae had been released by 1100 °C. In the marine alga, only around 20% of the total Cl was released below 500 °C with the majority being released above 850 °C. The fraction of S released at low temperatures was also lower when compared to the freshwater algae. Potassium and Na were more or less completely released from the marine alga by 1100 °C under pyrolysis and combustion conditions and by 1000 °C under gasification conditions. The release behavior of P was similar for all of the tested algae. Phosphorus release commenced around 850 °C under pyrolysis, combustion, and gasification atmospheres, and by 1100 °C, 40−70% of the total P had been released from the algae. Select ash residues were analyzed using X-ray diffraction and scanning electron microscopy, coupled with energy-dispersive spectroscopy, in order to gain insights into the release mechanisms. A two-step mechanism has been proposed for S release. The alkali metals and Cl were released proportionally from the marine alga but disproportionately from the freshwater algae. It is expected that K, Na, and Cl were released from the marine alga primarily by sublimation of alkali chlorides. Different mechanisms were responsible for the release of these elements from the freshwater algae. It has been suggested that Cl is dissociated from the alkali metals and then released as HCl vapor, and that K may be released by volatilization of melted K-phosphates. Sodium appeared to be released by similar mechanisms to K above 700 °C. The mechanisms governing the release of P are not entirely clear and require further investigation.

1. INTRODUCTION

Growing concern for future fuel security, brought about by continual depletion of nonrenewable fossil fuel reserves and an ever-increasing world population, has provided motivation for the development of alternate energy technologies. Technologies based on the sustainable use of biomass are playing a growing role in the global energy mix and are projected[1] to meet a significant portion of the total energy demand in the future. Both micro- and macroalgae are currently unexploited biomass which have several advantageous attributes as feedstocks for energy and fuel production. The production of algae has exceptional potential for high areal energy yields[2] and can be undertaken on nonarable land.[3] Algae can be cultivated in a diverse range of aquatic environments including both freshwater[4] and seawater[5] as well as various types of contaminated wastewater,[6] which opens up opportunities to combine the production of energy and fuels with bioremediation. Pyrolysis, combustion, and gasification are widely used thermal processes which can be used to convert dried algae to energy and fuels. It is also possible to convert algae when it is wet via oxidation or gasification in supercritical water.[7,8] However, current technologies based on these novel processes are not well-developed due to the extreme pressures required to achieve supercritical conditions.[9] In contrast, well-established technologies already exist for conventional thermal processes. Nevertheless, these established technologies are not without their limitations. They suffer from ash-related operational problems caused by inorganic impurities in the biomass.[10] The inorganic matter in biomass is responsible for fouling and deposition,[11] high temperature corrosion,[12] and, in the case of fluidized bed

Received: February 4, 2015
Revised: March 25, 2015
Published: March 26, 2015

ACS Publications © 2015 American Chemical Society

DOI: 10.1021/acs.energyfuels.5b00279
Energy Fuels 2015, 29, 2542−2554

Table 1. Summary of the Algal Samples Used in This Study

abbreviation	species	micro/macroalgae	water	added nutrients	harvest method
OD	*Oedogonium* sp.	macro	freshwater	desulfurized flue gas, f/2[a] medium	filtration, followed by centrifugation
TPC	polyculture dominated by *Schroederiella apiculata* and *Scenedesmus dimorphus*	micro	freshwater	desulfurized flue gas, f/2 medium	centrifugation
Tet	*Tetraselmis* sp.	micro	seawater	CO_2, $NaNO_3$, H_2PO_4	electroflocculation, followed by centrifugation

[a]A standard nutrient medium containing nitrate, phosphate, and various trace metals.

technologies, bed particle agglomeration[10] involving the sticking together of inert bed particles by various components in the ash. Consequences of ash-related problems include, but are not limited to, plugging of channels between boiler tubes,[13] erosion of gas turbine components,[14] and bed defluidization,[15] all of which can lead to expensive and unscheduled reactor shutdowns. Prior knowledge of the behavior of the inorganic matter is, therefore, essential before any new feedstock is utilized in thermal processes. Previous research on the thermal behavior of algal biomass has focused mainly on the conversion of the organic matter.[16−18] A number of recent studies have investigated the sintering tendencies and agglomerating behavior of algal ashes;[19−21] however, the relevance of these studies is mainly limited to fluidized bed technologies. It is clear that the current knowledge which addresses the behavior of the inorganic matter in algae during conventional thermal processes is limited, particularly with respect to ash-related problems.

There is a large body of knowledge dedicated to the behavior of the inorganic matter in terrestrial biomass and coal. Many studies have shown Cl, S, Na, K, and P to play key roles in ash-related problems. The alkali metals, Na and K, are notorious for forming low-temperature melting compounds which cause the formed ash to become sticky and prone to depositing on surfaces inside and downstream of the reactor. Chlorine is highly volatile in biomass.[22−25] It tends to mobilize the alkali metals[26] and accelerate high-temperature corrosion.[27] Sulfur is also highly volatile[23−25] and is capable of forming dense deposits.[28] The formation of molten sodium sulfates is known to be the root cause behind bed agglomeration during fluidized bed combustion of Na- and S-rich low-rank coals.[29,30] Phosphorus can contribute to ash deposition[31] and, when present in significant concentrations, bed agglomeration.[32] Chlorine, S, P, K, and Na are all present in high concentrations in algae and are expected to play important roles in ash-related problems.

The ultimate fate and role of the inorganic elements in ash-related problems is largely determined by the initial split between the solid and gas phase during fuel particle burnout.[10] The extent to which an inorganic element is released to the gas phase or is retained in the solid residue depends on both feedstock composition and on processing parameters such as reaction temperature and gas atmosphere. The importance of feedstock composition on the release of the inorganic elements is evident when comparing the behavior of the inorganic matter in different types of terrestrial fuels. Previous studies have focused on a broad range of terrestrial fuels including coal,[33−35] wood and wood-derived fuels,[23,36,37] agricultural residues,[24,25,38−40] grasses,[37,41,42] and sewage sludge.[43,44] There is generally good agreement in the literature for the mechanisms governing the release of Cl.[23−25,45,46] A useful schematic summarizing the different release pathways is provided by Johansen et al.[25] Several authors[41,47] have inferred that the release of S is affected by its occurrence mode in the fuel. Organic forms are thought to be released at low temperatures during the pyrolysis process,[41,47] involving the initial decomposition of the organic matrix. In combustion and gasification processes, pyrolysis is followed by a heterogeneous gas−solid reaction which involves oxidation or reduction of the residual organic matter (char). Inorganic forms of S are thought to be released during this latter phase of fuel particle conversion.[24,25,41] Literature on the release of P from terrestrial biomass[38,43,44] is relatively scarce. The release of the alkali metals, K and Na, is extremely complex and seems to be strongly influenced by the relative proportions of other inorganic elements in the fuel. A substantial amount of work has been done to understand the mechanisms governing the release of the alkali metals, and various authors[23−25] have attempted to summarize these mechanisms for a range of terrestrial fuels. Commonly reported mechanisms include vaporization of alkali salts (e.g., chlorides, sulfates, and phosphates), dissociation of alkali carbonates, alkali sulfates and alkali metals ion-exchanged to oxygen functionalities in the char matrix, and vaporization of alkali silicates. In many cases, the alkali metals are released by a combination of these mechanisms. The importance of a given mechanism is highly sensitive to feedstock composition and varies significantly from fuel to fuel. The composition of the inorganic matter in algae is distinctively different from both coal and terrestrial biomass, and the occurrence of the main inorganic elements in algae varies significantly for micro- and macroalgae species and for different culturing conditions.[19] Despite this, limited work has been done to characterize the release of Cl, S, P, K, and Na from algae or to understand how the release of these elements varies for different algal species and for different culturing environments.

The aim of this study was to characterize the release of Cl, S, P, K, and Na from a range of different types of algal biomass during thermal conversion. The first objective of this work was to determine the influence of algal properties, in terms of freshwater vs marine and macro vs micro, on the release of the inorganic elements under gas atmospheres relevant to pyrolysis, combustion, and gasification processes. The second objective was to provide insights into the mechanisms governing the release of the inorganic elements.

2. EXPERIMENTAL SECTION

2.1. Algal Samples. A diverse range of algae were selected for this work in order to assess the variability in the thermal behavior of the inorganic elements for different species and different culture environments. The selected samples (Table 1) are all grown for industrial applications. The freshwater macroalga, *Oedogonium* sp. (hereafter referred to as "OD"), and the freshwater polyculture of microalgae (hereafter referred to as "TPC") are key targets for broad spectrum bioremediation of waste waters.[48,49] The marine microalga, *Tetraselmis* sp. (hereafter referred to as "Tet") is a key species for biofuel production.[5] OD and TPC were grown in ash dam water at the Tarong coal-fired power station in Tarong, Queensland, and Tet was

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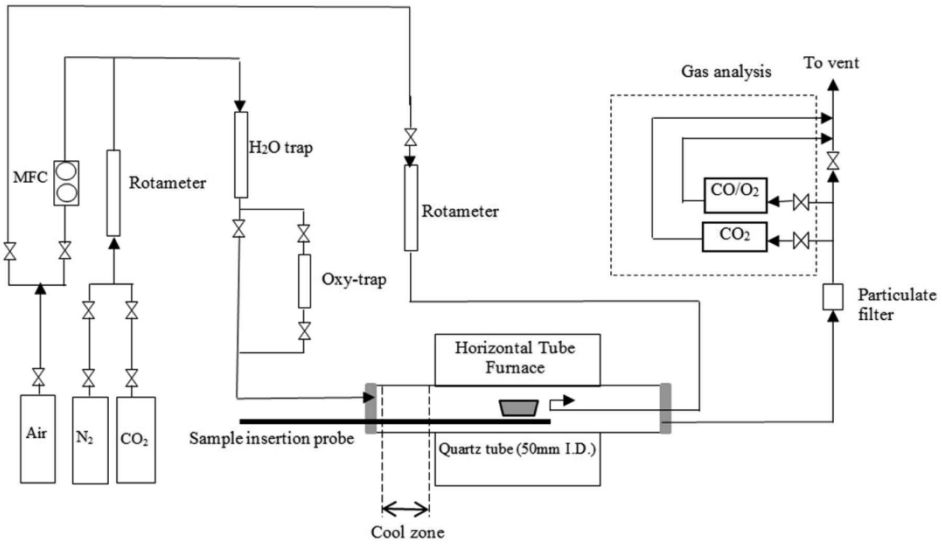

Figure 1. Schematic of the fixed-bed reactor setup used in the release experiments.

grown by Muradel Pty. Ltd. at their pilot plant in Karratha, Western Australia.

OD (genus *Oedogonium*, Genbank KF606974)[48] was isolated from the Tarong Ash Dam in October 2012 and then scaled up from small-scale cultures to large-scale cultures at James Cook University, Townsville. The scaled biomass was transported to Tarong in May 2013 and cultured directly in ash dam water which was pumped from the ash dam into a series of four 10 000 L culture tanks. The ash dam water was passed through a 10 μm filtration unit before being added to the culture tanks. Flue gas was piped directly from the power stations flue, through a desulfurization unit and into the bottom of the cultivation tanks to supply CO_2. The flue gas supply was linked to an in-line pH probe and set to maintain pH between 8.4−8.6 in the tanks. Nutrients were added as f/2 media,[50] a standard nutrient mix containing nitrate, phosphate, and various trace elements. Algae were grown under batch conditions, with 100% of the tank volume being harvested every 3−4 days. Harvests were carried out by draining the tanks through a hose into fabric bags which were then spun in a domestic washing machine for 7 min to remove excess water. TPC consists of a range of freshwater microalgae that were originally isolated from water samples collected from the Tarong power station. The polyculture is dominated by the green microalgae *Schroederiella apiculata* and *Scenedesmus dimorphus*. TPC was cultivated in covered, outdoor raceway ponds under ambient conditions. The raceway ponds received desulfurized flue gas, containing 20% CO_2, to maintain pH between 8.0 and 8.5, and the ash dam water was prefiltered as previously described for OD. Raceway ponds were harvested using a commercial centrifuge. Tet was cultivated in an outdoor, raceway pond and was harvested using an in-house electroflocculation process, followed by centrifugation. Detailed descriptions of the growth and harvesting methods used to produce OD and Tet can be found elsewhere.[16,49]

Harvested algal samples were air-dried (OD and TPC) or oven-dried at 45 °C (Tet) to a moisture content of less than 12 wt %. The microalgae (Tet and TPC) formed brittle aggregates when dried and the macroalgae (OD) coarse tufts of intertwined filaments. Samples were milled in a centrifugal knife mill and then sieved to obtain the 1.6−6.4 mm size fraction. This fraction was used in the release experiments. Samples of each alga were also milled to pass through a 250 μm screen. This size fraction was used for fuel analyses.

2.2. Reactor Setup. A laboratory-scale, fixed-bed, batch reactor was used to prepare char and ash samples from the algae. A schematic of the reactor setup is shown in Figure 1. The setup involved a 1.4 m long, 50 mm I.D., quartz tube which was positioned horizontally inside a 3-zone, electrically heated furnace so that the tube ends extended 40 and 50 cm from the front and back end of the furnace, respectively. Tapered silicone plugs were used to seal both ends of the quartz tube. A 1.0 m long alumina tube (I.D. 5 mm and O.D. 9 mm), featuring a flat platform cut-out at one end, was used as a sample insertion probe. Samples (1−4 g) were loaded into 20 mL alumina boats without compressing the fuel bed. The alumina boat was then secured to the insertion probe platform using molybdenum-based, temperature-resistant wire (diameter: 0.4 mm). A K-type thermocouple, which ran through the inside of the insertion probe tube, was used to monitor the temperature just under the sample boat. The reactor was designed so that the sample remained cool (<60 °C) and in an inert gas atmosphere while heating up the furnace. Preheated secondary air, introduced at a position just downstream of the sample, was used to oxidize volatiles released during pyrolysis so as to limit tar deposition at the outlet of the quartz tube.

High purity N_2, CO_2, and instrument grade air were used in the release experiments. All gases were fed from cylinders to the reactor via $^1/_4''$ nylon tubing. Reactant gases were first passed through a column packed with silica gel to remove any moisture. Nitrogen and CO_2 feed streams were also scrubbed of oxygen impurities using a commercially available oxy-trap. Rotameters were used to control the flow of N_2, CO_2, and secondary air. Gas phase residence times inside the reactor were around 30 s. A mass flow controller was used to control the flow of primary air. Product gases were passed through a quartz wool filter and monitored for O_2, CO, and CO_2 concentrations before being vented to exhaust. Two separate nondispersive infrared gas analysers were used to measure CO and CO_2 and a galvanic cell type analyzer to measure O_2.

2.3. Release Experiments. Release experiments were carried out under pyrolysis, combustion, and gasification conditions at various temperatures between 500 and 1100 °C. The residues were weighed at the end of each test and analyzed to determine the concentrations of Cl, S, K, Na, and P in the residues. Release of the inorganic elements from the algal samples was then calculated by mass balance according to eq 1

$$R_i\ (\%) = \left[1 - \frac{1}{(1-M)}\left(\frac{W_r}{W_A}\right)\left(\frac{C_{r,i}}{C_{A,i}}\right)\right] \times 100 \quad (1)$$

where R_i is the release of element i in weight percent, M is the moisture fraction of the algal feedstock (w/w), W_r and W_A are the

DOI: 10.1021/acs.energyfuels.5b00279
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weights (mg) of the residue and corresponding algal feedstock respectively, and $C_{r,i}$ and $C_{A,i}$ are the concentrations (w/w, dry basis) of element i in the residue and feedstock, respectively.

At the start of each experiment, gas flow rates were preset to their target values. The reactor was then purged with N_2 (4.0 L/min @ STP) while heating the furnace. Once the target furnace temperature had been reached, the sample was moved from the reactor inlet (cool zone) to the middle of the furnace. In the pyrolysis experiments, N_2 was fed to the reactor inlet at a flow rate of 4.0 L/min @ STP and secondary air was supplied at a flow rate of 2.0 L/min @ STP. Once pyrolysis had reached completion, the supply of secondary air was switched off. In combustion and gasification experiments, samples were first pyrolyzed as described for the pyrolysis experiments. This was done to prevent temperature overshoot caused by ignition of evolved volatiles. The residual organic matter was then oxidized or reduced by switching the gas atmosphere to 2% O_2/balance N_2 (combustion) or to CO_2 (gasification). Air was mixed with N_2 upstream of the reactor to create the target gas atmosphere for combustion experiments. Pyrolysis and combustion progress was tracked by monitoring the concentrations of CO and CO_2 in the product gases. Reactions were allowed to proceed until the concentrations of CO and CO_2 dropped below 50 and 200 ppmv, respectively. Only CO was monitored during gasification. Gasification times were constant for each algal sample and were selected based on the time taken for complete gasification of the sample at 850 °C, which was defined as the time taken for the concentration of CO in the product gases to drop below 50ppmv. Complete gasification took between 1.5 and 5 h for the different algal samples at 850 °C. Complete pyrolysis and complete combustion at 850 °C took between 15 min and 1 h and between 45 min and 2 h, respectively. At the end of each test, the gas atmosphere was switched back to N_2, the furnace heating elements switched off, and the sample retracted from the furnace to the cool zone of the reactor. Once the temperature of the sample boat dropped below 50 °C, the sample was removed from the furnace and the residue was weighed immediately. The residue was then crushed to a fine powder using a mortar and pestle and then stored in an airtight, plastic container for analysis. In order to avoid contamination between tests, the reactor was removed from the furnace and its interior was scrubbed in warm water at the end of each test. The reactor outlet was then heated in air (1000 °C) to burn off any tars which may have deposited on the tube walls during the previous test.

2.4. Analysis. Proximate and elemental compositions of the algal samples are presented in Table 2. Proximate composition was determined by thermogravimetric analysis (TGA). Samples were loosely packed into a cylindrical alumina crucible (I.D. 7 mm and height 1.2 mm) to approximately half-full. The crucible was then loaded into a TGA (Setaram Labsys). Samples were heated to 105 °C in N_2 (80 mL·min^{-1} @ STP) at a rate of 10 °C·min^{-1} and held at 105 °C for 30 min in order to remove residual moisture. Samples were then heated to 550 °C at a rate of 10 °C·min^{-1} and held at 550 °C for 1 h in order to determine the volatile matter content. The gas atmosphere was then switched to air in order to oxidize the remaining organic matter and determine the ash content. Fixed carbon content was calculated by difference.

Elemental composition was determined using a range of different methods. Carbon, H, and N were measured in triplicate using an elemental analyzer (LECO Truspec). Chlorine was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) using an Ar-filled, Spectro Ciros CCD (charged coupled device) in axial plasma viewing mode, following extraction in 4% v/v HNO_3. Details of this method can be found elsewhere.[51] Silicon was determined by ICP-OES, following borate fusion and acid dissolution. This method is based on Australian Standard AS 1038.14.1. Sulfur and all other inorganic elements, including K, Na, and P, were determined by ICP-OES, using a radial plasma viewing mode, following digestion in H_2O_2 (30% v/v)/HNO_3 (68% v/v)/HF (48% v/v). Samples (100 mg) were digested in 15 mL, flat-bottom, Teflon containers for a period of 12 h at a temperature of 140 °C using 0.6, 1.6, and 0.2 mL of H_2O_2, HNO_3, and HF, respectively. After 12 h of digestion, samples were evaporated to incipient dryness and the digestion was repeated. Digested samples were diluted in 5% v/v HNO_3 using plasticware so that the concentrations of the inorganic elements in the diluted samples were within the linear calibration range of the ICP-OES instrument. All plasticware was cleaned before use by soaking in a 3 M solution of HCl for a period of at least 12 h. Solution ICP-OES measurements were performed externally by HRL Technology Pty. Ltd. and Waite Analytical Services. For each batch of analysis, one blank and a certified plant reference material (U.S. National Institute of Standards and Technology, Gaithersburg, MD, USA) were analyzed in addition to the unknown samples. The concentrations of Cl, S, P, K, and Na in the algal sample OD were analyzed in quadruplicate in order to estimate the error in the measurement of these elements. Errors (95% confidence interval) were 5.4, 6.2, 6.2, 5.8, and 2.6% for Cl, S, P, K, and Na, respectively.

Scanning electron microscopy, coupled with energy-dispersive spectroscopy (SEM/EDS), and powder X-ray diffraction (XRD) were used to aid interpretation of the results. The morphology and composition of combustion ashes prepared at a low (700 °C) and a high temperature (1100 °C) were studied using a Philips XL30 SEM equipped with EDS. Sample preparation involved mounting intact ash particles on stubs, followed by carbon coating. Mineralogical analyses were performed on each alga and on high-temperature (1100 °C) combustion ashes. Samples were oven-dried (80 °C) and then milled using a mortar and pestle before being pressed into stainless steel sample holders. XRD patterns were recorded using a PANalytical X'Pert Pro Multipurpose Diffractometer using Fe-filtered Co Kα radiation, an automatic divergence slit, 2° antiscatter slit, and fast X'Celerator Si strip detector. The diffraction patterns were recorded from 3° to 80° in steps of 0.017° 2θ with a 0.5 s counting time per step for an overall counting time of approximately 35 min. The XRD patterns were recorded and interpreted externally, by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) Division of Land and Water.

Table 2. Proximate and Elemental Compositions of the Tested Algae

algae	OD	TPC	Tet
	proximate composition (wt %)		
moisture[a]	7.3	10.8	6.4
volatile matter[b]	58.7	57.7	35.5
fixed carbon[b]	20.4	19.0	5.9
ash[b]	20.9	23.3	58.6
	elemental composition (wt %)[b]		
C	34.8	41.3	17.0
H	5.0	5.8	3.3
N	5.4	6.9	2.5
S	0.53	1.01	2.10
Cl	0.25	0.50	17.62
P	1.37	1.36	0.25
Na	0.23	0.51	10.86
K	1.08	0.59	1.03
Ca	1.00	1.67	2.50
Mg	0.26	0.34	1.86
Si	7.55	6.99	0.68
Fe	1.60	0.44	0.30
Al	0.35	0.21	6.17
Ti	0.0102	0.0062	0.0170

[a]After drying. [b]Dry basis.

3. RESULTS AND DISCUSSION

The Results and Discussion section consists of three parts: (1) release profiles for Cl, S, P, K, and Na, (2) SEM/EDS and XRD analyses of algal ashes, and (3) a discussion on the release mechanisms.

DOI: 10.1021/acs.energyfuels.5b00279
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3.1. Release Profiles. The release profiles are based on elemental analyses of char and ash samples prepared under pyrolysis, combustion, and gasification conditions at various temperatures between 500 and 1100 °C. The profiles are presented in Figures 2−6 and were used to determine the influence of algal type, in terms of micro vs macro and freshwater vs marine, on the release of the inorganic elements. Note that data is not presented for gasification of OD and TPC at 500 °C or for gasification of Tet at 500 and 700 °C since the algal chars were barely reactive under these conditions. Errors in the calculated release values are presented for OD under pyrolysis conditions in Figures 2−6 and were found to diminish with increasing release. It is expected that the errors would have followed a similar trend for the different gas atmospheres and for each of the tested alga. The errors were estimated by propagation of the errors in the elemental concentration measurements and the algal moisture content measurements which were based on two standard deviations of the measured quantities.

Chlorine. The freshwater algae (OD and TPC) both display similar Cl-release behavior (see Figure 2). Over half of the Cl in OD and TPC is released by 500 °C and virtually all of the Cl is released by 1000 °C under pyrolysis conditions. Under combustion and gasification conditions, complete release of chlorine is shifted toward lower temperatures (700 °C). Differences in the behavior of Cl under combustion and gasification conditions are minor. Interestingly, the release profiles for OD and TPC closely resemble that of corn stover,[25] which has a similar Cl content to the two freshwater algae (0.25 and 0.50 wt %, dry basis). The behavior of Cl in the marine alga, Tet, is significantly different to that of the freshwater algae, which is not surprising, given that there is over an order of magnitude more Cl in Tet. In Tet, a lower proportion of the total Cl is released below 500 °C (around 20%) and complete release of Cl occurs between 1000 and 1100 °C under pyrolysis, combustion, and gasification conditions.

Sulfur. The majority of S (>70%) in OD and TPC is released by 500 °C during pyrolysis (see Figure 3). The low-temperature release from Tet on the other hand is much lower (around 30%). There is only a gradual increase in the release of S from all of the tested algae under pyrolysis conditions with increasing temperature above 500 °C. Combustion and gasification atmospheres on the other hand result in an additional release of S above 500 °C. In the case of OD and TPC, complete desulfurization occurs by 850 °C under both combustion and gasification conditions. Complete desulfurization of Tet occurs around 1100 °C during combustion and 850 °C during CO_2 gasification.

Phosphorus. The release profiles for P (Figure 4) are similar for all of the tested algae. Very little of the total P (<10%) is released below 850 °C, indicating that the onset of P release occurs above 850 °C. The slightly negative release values reported for TPC and Tet are likely due to inhomogeneities in fuel composition but may also be due to errors in the measurement of P. Increasing temperature above 850 °C causes an increase in the release of P. By 1100 °C, between 40% and 70% of the total P is released to the gas phase. These values are similar to P-release data reported by Wu et al.[38] during bran combustion in a fixed-bed reactor at 1100 °C. The different gas atmospheres were found to have only a minor effect on the release of P from the algae.

Potassium. Low levels of K (2−12%) are released below 700 °C from each of the tested algae (see Figure 5). Above 700 °C,

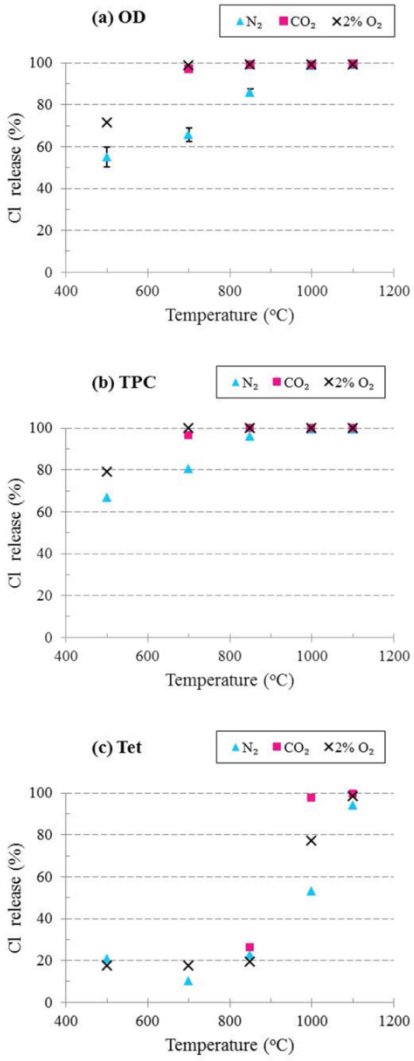

Figure 2. Release to the gas phase of Cl from OD (a), TPC (b), and Tet (c) as a function of reactor temperature. Release data are presented for pyrolysis (N_2), combustion (2% O_2/balance N_2), and gasification (CO_2) gas atmospheres. Note that data is not shown for CO_2 at 500 °C in (a) and (b), and at 500 and 700 °C in (c).

K is released gradually from OD and TPC and seems to be unaffected by differences in gas atmosphere. Only 20−35% of the total K in OD and TPC is released by 1100 °C. These values are relatively low when compared to K-release data reported in the literature for different types of terrestrial biomass.[25,38,39] The high-temperature release (>700 °C) of K is much greater from Tet. Over 60% of the total K in Tet is released by 1000 °C and virtually all K is released by 1100 °C under pyrolysis and combustion conditions. Complete release of K is shifted toward slightly lower temperatures (1000 °C) under gasification conditions. The more pronounced release of K under gasification conditions may be due to differences in the reactivity of Tet char particles under reducing and oxidizing gas atmospheres. The rate of char conversion under combustion

DOI: 10.1021/acs.energyfuels.5b00279
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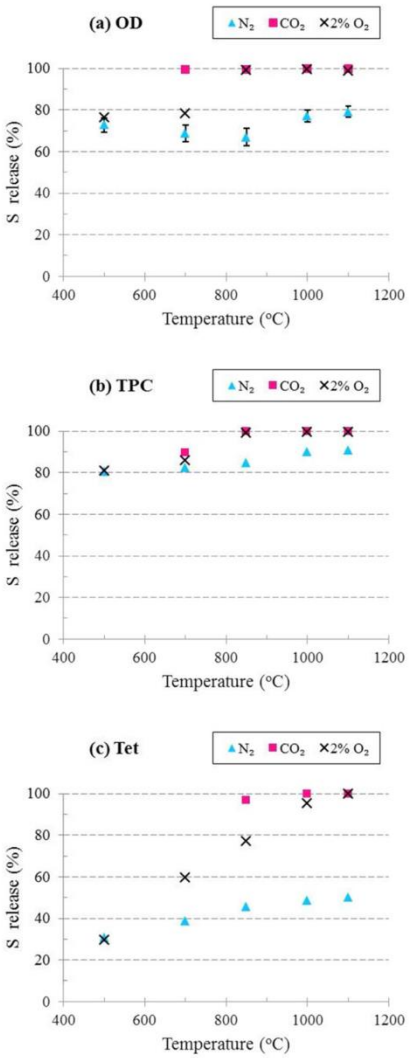

Figure 3. Release to the gas phase of S from OD (a), TPC (b), and Tet (c) as a function of reactor temperature. Release data are presented for pyrolysis (N_2), combustion (2% O_2/balance N_2), and gasification (CO_2) gas atmospheres. Note that data is not shown for CO_2 at 500 °C in (a) and (b), and at 500 and 700 °C in (c).

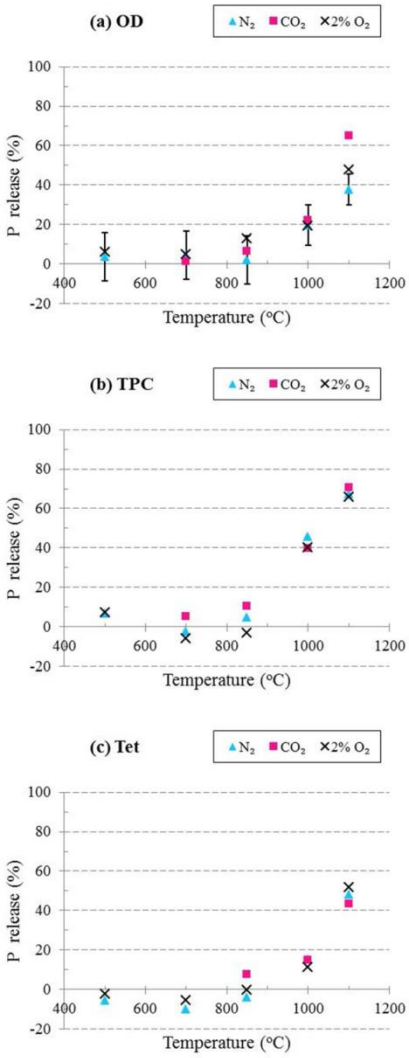

Figure 4. Release to the gas phase of P from OD (a), TPC (b), and Tet (c) as a function of reactor temperature. Release data are presented for pyrolysis (N_2), combustion (2% O_2/balance N_2), and gasification (CO_2) gas atmospheres. Note that data is not shown for CO_2 at 500 °C in (a) and (b), and at 500 and 700 °C in (c).

conditions is likely mass-transport limited for temperatures above 850 °C and for char particles of the order of 1 mm in size.[52] Combustion reactions are, therefore, likely to be concentrated at the surface of the char particles, which hinders pore development.[53] Chemical reactions are much slower in CO_2 (gasification)[53] and presumably take place deeper within the internal pores of the char particle. This promotes pore enlargement through product gas evolution inside the particle itself. The formation of larger pores during gasification could lead to lower K vapor pressure within the pores and consequently enhance the rate of K volatilization from the char. A similar rationale has been suggested[54] for the high release of Na during gasification of brown coal.

Sodium. Release of Na (Figure 6) below 700 °C ranges between 10% and 25% and seems to be unaffected by differences in gas atmosphere. The low-temperature release of Na (<700 °C) is on average greater than that of K. Interestingly, van Lith et al.[23] also reported a greater low-temperature release of Na than K during combustion of wood-derived fuels in a reactor setup similar to the one used in this study. The behavior of Na closely resembles that of K within the temperature interval of 700−1100 °C for all of the tested algae.

3.2. SEM/EDS and XRD Analyses. SEM images of algal combustion ashes prepared at both low (700 °C) and high (1100 °C) temperatures are presented in Figures 7−9 for OD, TPC, and Tet. Also presented in Figures 7−9 are the bulk compositions of the ashes determined using EDS. The low-temperature ashes of OD (see Figure 7a) and TPC (see Figure 8a) contain separate seed-like particles, 10−30 μm in size.

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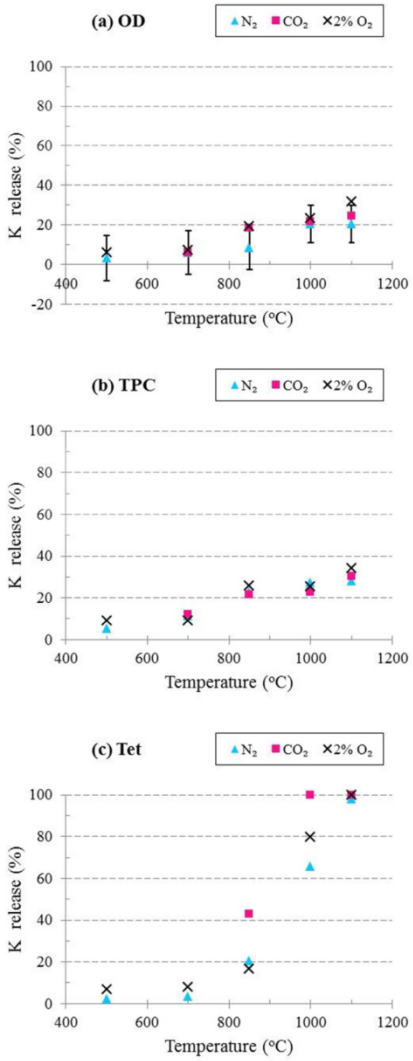

Figure 5. Release to the gas phase of K from OD (a), TPC (b), and Tet (c) as a function of reactor temperature. Release data are presented for pyrolysis (N_2), combustion (2% O_2/balance N_2), and gasification (CO_2) gas atmospheres. Note that data is not shown for CO_2 at 500 °C in (a) and (b), and at 500 and 700 °C in (c).

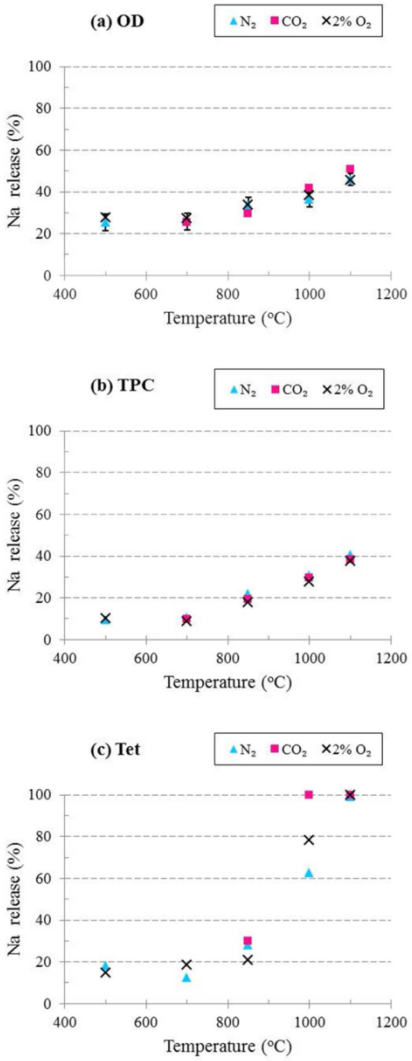

Figure 6. Release to the gas phase of Na from OD (a), TPC (b), and Tet (c) as a function of reactor temperature. Release data are presented for pyrolysis (N_2), combustion (2% O_2/balance N_2), and gasification (CO_2) gas atmospheres. Note that data is not shown for CO_2 at 500 °C in (a) and (b), and at 500 and 700 °C in (c).

Their high-temperature ashes (see Figures 7b and 8b), on the other hand, consist of large, smooth blocks, which suggest that the ash particles fuse together above 700 °C, possibly via the formation of molten ash. The ashes of OD and TPC are dominated by Si (see Figures 7c and 8c), which could be expected given the substantial Si contents (7−8 wt %, dry basis) in these algae and the refractory nature of Si at temperatures below 1100 °C.[55] Phosphorus concentrations in the ashes of OD and TPC were much lower, but still significant, particularly in the ashes of TPC. The low-temperature ashes of Tet are dominated by Al, Na, and Cl (see Figure 9c) and contain discrete cubic particles 2−8 μm in size (see Figure 9a). EDS point analyses were performed on several of these particles in order to determine their identity. The results are presented in Figure 9c. The particles consist almost exclusively of Na and Cl and are probably unreacted NaCl crystals which had precipitated from the algae during biomass drying. The cubic particles were not observed in the high-temperature ashes of Tet (see Figure 9b), and negligible levels of Na and much lower levels of Cl were detected in the ashes (see Figure 9c). This finding is consistent with the Na and Cl release profiles for Tet, which show these elements to be more or less completely released from Tet by 1100 °C. The high-temperature ashes of Tet consist mainly of Al but also contain significant levels of Ca and Mg (see Figure 9c). The Al in Tet is introduced to the alga as aluminum hydroxide[56] during the harvesting process, which involves flocculating algae from the growth medium by applying an electric current to sacrificial aluminum electrodes, which provide ions for flocculation.[16]

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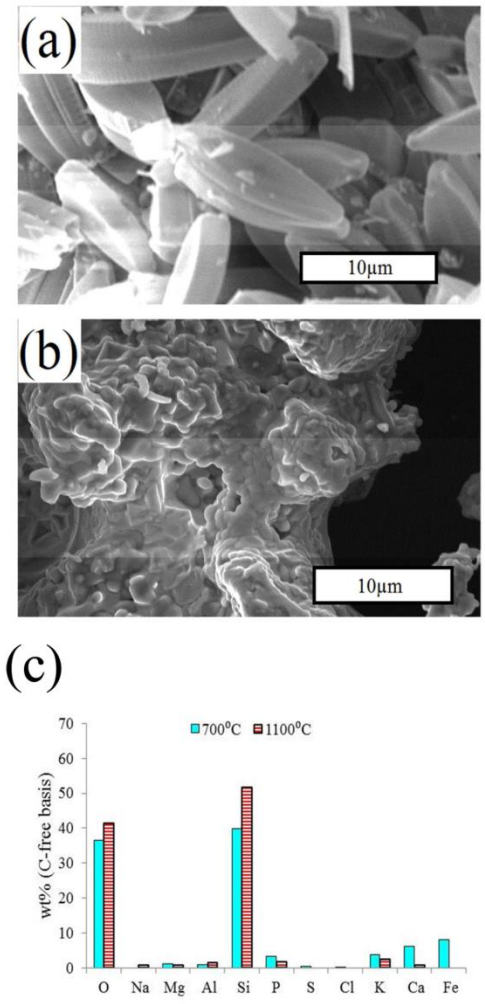

Figure 7. SEM images of OD combustion ashes prepared at 700 °C (a) and 1100 °C (b). (c) Elemental composition of the ashes determined using EDS.

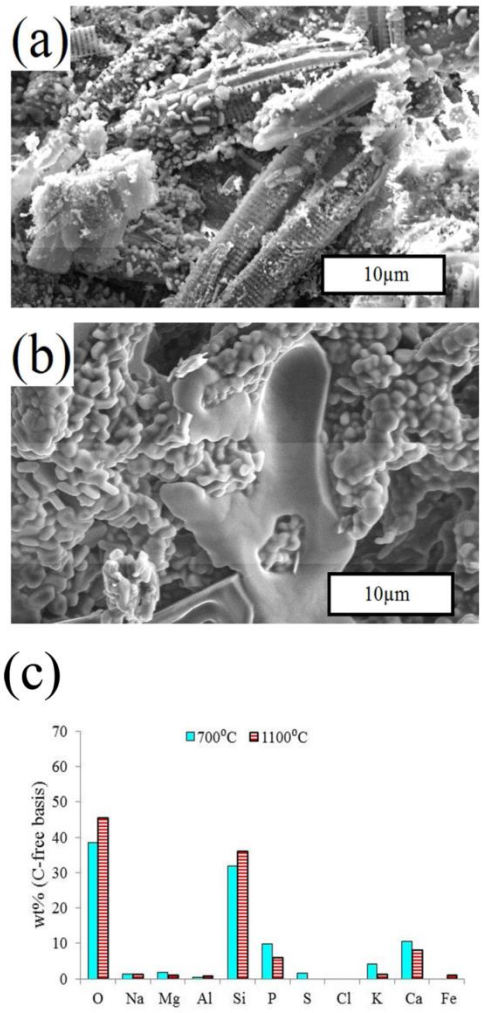

Figure 8. SEM images of TPC combustion ashes prepared at 700 °C (a) and 1100 °C (b). (c) Elemental composition of the ashes determined using EDS.

Mineralogical analyses were conducted using XRD. The analyses are presented in Table 3 for combustion ashes prepared at 1100 °C and for the corresponding algal feedstocks. Cristobalite (SiO_2) was identified as a dominant phase in the ashes of OD and TPC and spinel ($MgAl_2O_4$) as a dominant phase in the ashes of Tet. These findings are in agreement with the SEM/EDS analyses, which show Si to be a main component of the high-temperature ashes of OD and TPC, and Al and Mg to be major components in the high-temperature ashes of Tet. Halite (NaCl) was identified as dominant in Tet but was not identified in the combustion ashes of Tet. This finding provides further evidence that Na and Cl are more or less completely released from Tet at high temperatures.

3.3. Release Mechanisms. An interpretation of the release profiles is presented in this section in terms of the governing release mechanisms. The interpretation was supported by (1) the SEM/EDS and XRD analyses presented in section 3.2, (2) a review of the literature on the mechanisms responsible for the release of inorganic elements from terrestrial biomass, and (3) consideration of the occurrence modes of the main inorganic elements in algae.

Chlorine is almost certainly present in dried algal biomass as precipitated alkali chlorides.[19] Release of Cl from alkali chlorides is understood to take place via two separate mechanisms during thermal conversion of terrestrial fuels.[22,24,25] Mechanism (1) probably commences at around 300 °C[22] and involves incorporation of the alkali metal into proton donor sites in the char matrix (e.g., carboxylic groups)[46,57] and the simultaneous release of Cl to the gas phase as HCl. Mechanism (2) involves the sublimation of alkali chlorides and becomes significant at temperatures above 700 °C. The principal mechanism of release seems to depend on the absolute Cl content of the fuel. For Cl-lean fuels (<0.6 wt % Cl) such as wood,[23] mechanism (1) tends to dominate. For Cl-rich fuels (>0.6 wt % Cl) such as barley,[24] mechanism (2) tends to dominate since release by mechanism (1) is limited by the availability of proton donor sites in the char matrix for alkali

DOI: 10.1021/acs.energyfuels.5b00279
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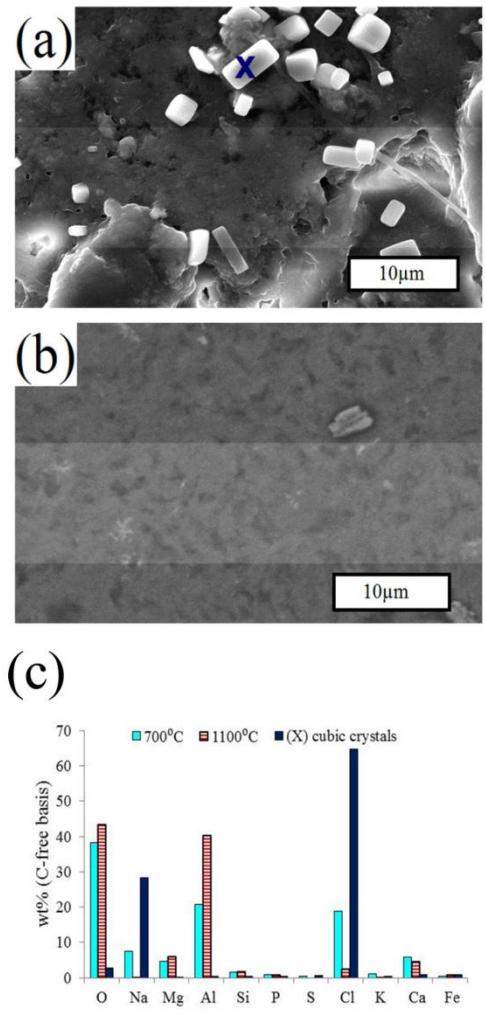

Figure 9. SEM images of Tet combustion ashes prepared at 700 °C (a) and 1100 °C (b). (c) Elemental composition of the ashes determined using EDS. Also shown in (c) is the average composition of the cubic crystals in (a), which was determined by performing EDS point analyses on 8 different crystals. An example of a cubic crystal in (a) is identified with an (X).

capture. A comparison of the absolute release of the alkali metals and Cl from the tested algae during combustion is presented in Figure 10. Results are expressed as mmol per gram of dry algae. The majority of the Cl in the freshwater algae, OD, and TPC, is released by 500 °C, and the release of Cl is disproportionate to the release of the alkali metals. It is, therefore, expected that mechanism (1) is the principal mechanism governing the release of Cl from these algae. The marine alga, Tet, contains extremely high levels of NaCl (around one-quarter of the biomass by weight) and low levels of fixed carbon (5.9 wt %, dry basis), which indicates that the number of sites in the char for Na capture, required for release by mechanism (1), would be extremely limited. There is substantial evidence that mechanism (2) dominates in the case of Tet. The release of Cl is relatively low from Tet below 700 °C (<20%), and there is a striking correlation between the release of the alkali metals and Cl with increasing temperature (see Figure 10c). On top of this, NaCl crystals were identified in Tet combustion ashes prepared at 700 °C.

The high release of S from OD and TPC (65−90% of the total fuel-S) during pyrolysis indicates that a large portion of the S in these algae is released during initial decomposition of the organic matrix. Lower levels (30−50%) of S are released from Tet during pyrolysis. Sulfur occurs in algae in both organic and inorganic forms.[58] It is possible that differences in the proportions of these two forms in the freshwater algae and Tet could account for the different fractions of S released during pyrolysis. Inorganic $CaSO_4$ was identified as trace in the XRD spectrum for Tet but not in the spectra for OD and TPC (see Table 3). Furthermore, in previous work,[19] we compared the leaching behavior of S in Tet to that in freshwater algae. The water-soluble fraction was found to be greater in Tet than in the freshwater samples. This could imply that there is less organically associated S in Tet and, therefore, explain the lower release of S from Tet during pyrolysis. An additional release of S takes place after pyrolysis, during the char oxidation/reduction phase of fuel particle conversion. Note that this additional release is relevant to combustion and gasification processes only. In the case of OD and TPC, it is unlikely that alkali sulfate vaporization accounts for the additional release of S given the high melting points of Na_2SO_4 and K_2SO_4 (884 and 1069 °C, respectively[59]) and that desulfurization is more or less complete by 850 °C under combustion and gasification conditions. Instead, decomposition of metal sulfates involving the release of SO_2 (combustion[33,41,47]) or H_2S and COS (gasification[33,37]) to the gas phase, is expected.

The extent of S retention in the char/ash residues is closely linked to the availability of base cations, particularly the alkali and alkaline earth metals.[24,47] Sulfur that has been released to the gas phase may even be recaptured in the fuel bed by base cations.[24] The availability of the base cations in terrestrial

Table 3. XRD Analyses for the Tested Algae and Their Combustion Ashes (1100 °C)[a]

sample	dominant	minor	trace
OD	amorphous material		halite (NaCl) and possible quartz (SiO_2)
TPC	amorphous material		anorthite ($CaAl_2Si_2O_8$) and quartz (SiO_2)
Tet	halite (NaCl)	amorphous material	quartz (SiO_2), gypsum ($CaSO_4{\cdot}2H_2O$), and basanite ($CaSO_4{\cdot}0.5H_2O$)
OD ashes	cristobalite (SiO_2)	powellite ($CaMoO_4$)	quartz (SiO_2), halite (NaCl), and hematite (Fe_2O_3)
TPC ashes	cristobalite (SiO_2) and powellite ($CaMoO_4$)	augite [$Ca(Mg,Fe)Si_2O_6$] and apatite [$Ca_5(PO_4)_3(Cl,F)$]	hematite (Fe_2O_3) and quartz (SiO_2)
Tet ashes	spinel ($MgAl_2O_4$) and powellite ($CaMoO_4$)		corundum (Al_2O_3), anorthite [$(Ca,Na)(Al,Si)_2Si_2O_8$], quartz (SiO_2), and cristobalite (SiO_2)

[a]The approximate abundance of each phase is indicated by the following ranges: dominant (>60%), co-dominant (sum >60%), minor (5-20%), and trace (<5%).

DOI: 10.1021/acs.energyfuels.5b00279
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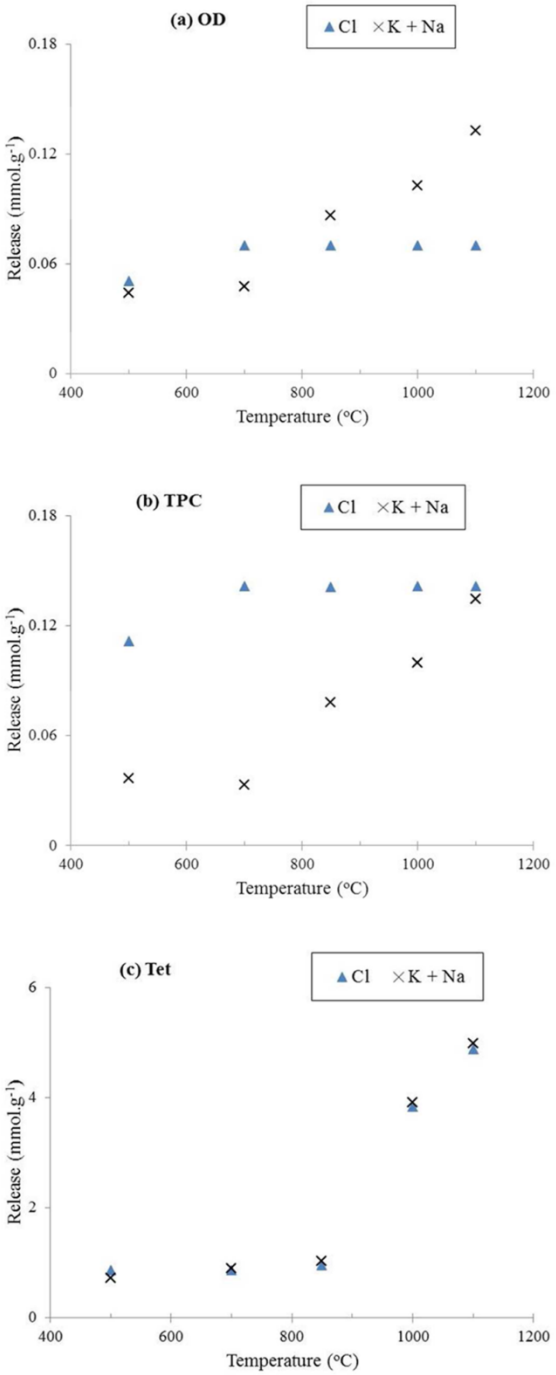

Figure 10. Absolute release of the alkali metals and Cl from OD (a), TPC (b), and Tet (c) during combustion in 2% O_2/balance N_2. Results are expressed in mmol·g^{-1} of dry algae. The scale on the *y*-axis for Tet is higher to account for the greater levels of Na and Cl in Tet.

biomass for S retention is limited by the formation of alkali and alkaline earth metal silicates.[24] Phosphorus has a greater affinity for the base cations than does S[60] and, therefore, might also limit the potential for S retention. In algae, P and Si are present in significant concentrations and are both expected to affect the potential for S retention. Sulfur is completely released to the gas phase during combustion of OD and TPC at 850 °C, whereas S is partially retained in the ashes of Tet during combustion under the same conditions. It is expected that differences in the proportions of the inorganic elements in the freshwater algae and Tet account for the differences in S-release behavior during combustion. The two freshwater algae (OD and TPC) contain relatively high proportions of P and Si compared to the base cations. The converse is the case for Tet. These differences in chemical composition are shown schematically in Figure 11. Terrestrial biomass fuels studied by Knudsen et al.,[24] which have proportions more similar to Tet than the freshwater algae, are also included in Figure 11 for comparison.

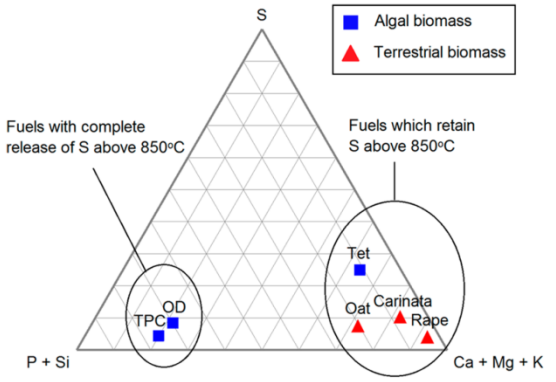

Figure 11. Compositional triangle (weight percent) of the system (P + Si) − S − (Ca + Mg + K). The algal samples are compared to terrestrial biomass fuels studied by Knudsen et al.[24] in terms of their S-release behavior.

The mechanisms governing the release of P from biomass are not well-understood. Wu et al.[38] proposed that P is released during bran combustion via the formation of molten phase phosphate compounds, followed by vaporization of KPO_3. It is possible that a similar mechanism, involving the formation of a phosphate melt, is responsible for the release of P from algae. In a previous study on the agglomerating behavior of algal ashes,[19] P was found concentrated in smooth globules inside the ashes (850 °C) of *Oedogonium*, which indicates the formation of molten phase phosphate compounds during combustion. According to the mechanism proposed by Wu et al.,[38] the release of P is dependent on the melting behavior of phosphate species in the ashes, which is largely controlled by the amount of alkaline earth metals, Ca and Mg, in the ashes.[31,61,62] In general, the melting behavior of phosphate compounds is shifted toward higher temperatures, the greater the alkaline earth metal content. The tested algae all contain relatively high levels of Ca and Mg (1.3−3.5 wt %, dry basis), which may explain why P is partially retained in the char/ash residues at temperatures below 1100 °C. Interestingly, the P-containing mineral, apatite [$Ca_5(PO_4)_3$], was identified in the high-temperature ashes (1100 °C) of TPC but not in the ashes of OD and Tet. There is no clear correlation between the release of P and the release of the alkali metals, K and Na, from the tested algae. Phosphorus release from OD and TPC is much more sensitive to increases in temperature within the

DOI: 10.1021/acs.energyfuels.5b00279
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temperature interval of 850−1100 °C than the release of the alkali metals. It is, therefore, difficult to infer from the release profiles what species P is being released as from the algae. The measurement of P-containing species in the gas phase may help to make this clear and is recommended for future work.

In terrestrial biomass, the low-temperature release of K (<700 °C) is thought to be due to decomposition of organically associated K during pyrolysis.[39,63,64] It is likely that this is also the case for algae, given that only a small amount of the total K (<10%) is released below 700 °C (see Figure 5) and that only a minor portion of the total K in algae is organically associated (estimated to be around 10% based on chemical fractionation analyses of various algal samples[19]). In the case of Tet, there is a striking correlation between the release of Cl and the release of K above 700 °C, as can be seen by comparison of Figures 2c and 5c. It is, therefore, expected that sublimation of KCl is the main mechanism governing the high-temperature release of K from Tet. The mechanisms responsible for the release of K from OD and TPC above 700 °C are less clear. Sublimation of KCl is unlikely to be significant, given that K is present in stoichiometric excess to Cl in the algae and that the vast majority of Cl is released from these algae below 700 °C. Vaporization of K_2SO_4 is not significant below 1000 °C, according to Knudsen et al.,[24] and is, therefore, also considered unlikely given that desulfurization of OD and TPC is complete by 850 °C under combustion and gasification conditions. Vaporization of melted K-phosphates, particularly KPO_3 and $CaK(PO_3)_3$, which have melting points of 810 and 846 °C, respectively,[62] could be expected, given the high affinity of K for P in thermal processes[60] and the significant release of P from algae above 850 °C. It is well-known that the alkali metals can undergo various transformations during thermal processes. Potassium may also be partially released from OD and TPC by decomposition of potassium carbonates and sulfates even if these compounds are not initially present in the algae.

The behavior of Na during thermal conversion has been studied in depth in brown coal[34,35,57,65,66] and to a much lesser extent in terrestrial biomass.[23,39,55] Most authors report only a minor release of Na at low-temperatures (<700 °C); however, a few studies[23,39] have reported significant release at temperatures as low as 500 °C. In algae, a significant fraction (10−25%) of the total Na is released below 500 °C. It has been suggested in the literature,[39,67] but not definitively proven, that the low-temperature release of Na is a result of detachment of sodium carboxylate from the organic matrix during pyrolysis. Sodium is almost exclusively water-soluble in algae[19] and presumably occurs as NaCl. On heating, NaCl partly dissociates[65,68] and some Na may be converted into organic forms.[65] It is, therefore, possible that volatilization of carboxylate sodium could cause Na to be released from algae at low temperatures. However, in the case of Tet, it is considered highly unlikely that this mechanism accounts for all of the Na released at low temperatures, given the substantial level of Na (10.9 wt %, dry basis) and the relatively low level of fixed carbon (5.9 wt %, dry basis) in Tet. Chlorine and the alkali metals, Na and K, are released proportionally from Tet below 700 °C (see Figure 10c); however, the exact mechanisms governing the low-temperature release of Na are not entirely clear. Many of the mechanisms reported in the literature for Na release above 700 °C are similar to those reported for K release. NaCl sublimation[42,66] and sodium carbonate decomposition[23,66] have been suggested by a number of authors. In many brown coals, Na is released disproportionately to Cl.[34,68] Kosminski et al.[66] identified sodium carbonate in the residual char after pyrolysis of a Victorian brown coal and proposed that Na is released in elemental form from the char as a result of carbonate decomposition. Dayton et al.[42] measured alkali vapor species released during combustion of Cl-rich switchgrass using molecular beam sampling/mass spectrometry and found NaCl to be the primary Na-containing species. In algae, the release profiles for Na closely resemble that of K within the temperature interval of 700−1100 °C. It is, therefore, expected that Na is released by mechanisms similar to those described for K above 700 °C.

Around 65−80% of the total K and around 50−65% of the total Na in OD and TPC are retained in the char and ash residues (see Figures 5a,b and 6a,b) at temperatures as high as 1100 °C. The alkali metals in Tet, on the other hand, are almost completely released to the gas phase at such high temperatures (see Figures 5c and 6c). The extent of release of the alkali metals during thermal conversion has been found to vary significantly in different types of terrestrial biomass.[23−25,39] Knudsen et al.[24] compared the release of K from annual biomass with different chemical compositions and concluded that the compositional parameters K/Cl and K/Si have significant influence on the retention of K. It is understood that K is preferentially released in the form of KCl until Cl becomes limiting. The release of the remaining K depends on the availability of Si to form nonvolatile silicates in the char and ash residues. Both potassium and sodium silicates have been identified in the ashes of biomass[24,69] and coal.[70] In Tet, the molar ratio Cl/(Na + K) is almost exactly 1:1 and it is, therefore, likely that there is sufficient Cl to enable complete release of the alkali metals as alkali chlorides. During thermal conversion of OD and TPC, on the other hand, Cl becomes deficient and no doubt limits the release of the alkali metals as alkali chlorides. It is possible that a significant portion of the total K and Na is incorporated into nonvolatile silicates, given the high concentrations of Si found in the combustion ashes of OD and TPC. Formation of nonvolatile alkali phosphates may also play a role in inhibiting the release of the alkali metals.

4. CONCLUSIONS

Differences in the release of Cl, S, K, and Na between the freshwater microalgae and the freshwater macroalga were found to be minor. The majority of Cl is released from the freshwater algae below 500 °C, and dechlorination is complete by 1000 °C under pyrolysis conditions and by 850 °C under combustion and gasification conditions. The majority of the S in the freshwater algae is released during pyrolysis at low temperatures. The remaining S is released with increasing temperature under combustion and gasification conditions but is partially retained in the char residue under pyrolysis conditions. The release of K is low (<10%) below 700 °C. The proportion of total Na released at low temperatures is slightly higher (10−25%). Potassium and Na are released gradually from the freshwater algae with increasing temperature above 700 °C. At least half of the initial Na and K are retained in the char and ash residues at 1100 °C. The release of K and Na from the freshwater algae is similar under pyrolysis, combustion, and gasification conditions. Substantial differences in the release of Cl, S, K, and Na were found when comparing the marine alga to the freshwater algae. A much lower proportion of the fuel-Cl is released from the marine alga at low temperatures (<500 °C) with the majority being released above 850 °C. There is a strong correlation between the release of Cl and the release of

DOI: 10.1021/acs.energyfuels.5b00279
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the alkali metals, Na and K, from the marine alga. Chlorine, K, and Na are substantially released by 1100 °C under pyrolysis and combustion conditions and by 1000 °C under gasification conditions. The release of P is similar for all of the tested algae under pyrolysis, combustion, and gasification conditions. The onset of P release occurs at around 850 °C, and between 40% and 70% of the fuel-P is released by 1100 °C.

Possible release mechanisms for each of the main inorganic elements are proposed. Chlorine appears to be released together with the alkali metals from the marine alga, primarily by sublimation of NaCl. In the freshwater algae, Cl is present in much lower proportions and is mainly released separately from the alkali metals, presumably in the form of HCl. Sulfur is released in two stages. It is proposed that organic forms are released first as part of the pyrolysis process and inorganic forms are released later during oxidation or reduction of the residual char. Sulfur is released from the freshwater algae at lower temperatures than K and Na. Vaporization of alkali sulfates is considered unlikely. The mechanisms governing P release are not clear. It is suggested that molten phase phosphates are formed in the char and ash residues and are then evaporated. Sublimation of KCl appears to be the primary release mechanism for K in the marine alga. Potassium is released from the freshwater algae by different mechanisms. Volatilization of melted K-phosphates is suggested. It is expected that Si plays a key role in inhibiting the complete release of K from the freshwater algae. Sodium appears to be released by similar mechanisms to K at temperatures above 700 °C. An additional low-temperature mechanism is also responsible for the release of Na.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: daniel.lane@adelaide.edu.au (D.J.L.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

David Bruce is gratefully acknowledged for his advice in analytical aspects of this work. This work was supported by the Australian Research Council's Linkage Projects funding scheme (project number LP100200616) with our industry partner SQC Pty. Ltd., the Australian Government through the Australian Renewable Energy Agency (funding agreement number Q00150), and the Advanced Manufacturing Cooperative Research Centre, funded through the Australian Government's Cooperative Research Centre Scheme. The authors also wish to acknowledge the support of Muradel Pty Ltd. and MBD Energy.

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DOI: 10.1021/acs.energyfuels.5b00279
Energy Fuels 2015, 29, 2542−2554

Chapter 6

Paper IV

Mobilisation of Trace Elements during Thermal Conversion of Algae Cultivated in Ash Dam Water

Daniel J. Lane[a], Philip J. van Eyk[a], Rocky de Nys[b], David A. Roberts[b], Andrew J. Cole[b], and Peter J. Ashman[a]

[a]School of Chemical Engineering, The University of Adelaide, Adelaide, South Australia 5005, Australia

[b]MACRO – the Centre for Macroalgal Resources and Biotechnology, College of Marine and Environmental Sciences, James Cook University, Townsville, Queensland 4811, Australia

Biomass & Bioenergy **2015**, 83, pp. 183 – 195.

Statement of Authorship

Publication Details: Lane DJ, van Eyk PJ, de Nys R, Roberts DA, Cole AJ, Ashman PJ. Mobilisation of trace elements during thermal conversion of algae cultivated in ash dam water. Biomass & Bioenergy 2015, In Press.

Publication status: In Press (accepted for publication 28/09/2015)

Author contributions:

By signing the Statement of Authorship, each author certifies that their stated contribution to the publication is accurate and that permission is granted for the publication to be included in the candidate's thesis.

Daniel J. Lane (Candidate)
Under the supervision of P. J. van Eyk and P. J. Ashman, I designed and performed the experiments, interpreted and processed the data, and wrote the manuscript.

Signed Date 16/10/2015

Philip J. van Eyk
I supervised the candidate, aided in the development of the experimental method, aided in the interpretation of the data, and evaluated the final version of the manuscript.

Signed Date 16/10/15

Rocky de Nys
I coordinated the cultivation of biomass for the experiments and evaluated the final version of the manuscript.

Signed Date 22/10/15

David A. Roberts
I cultivated biomass for the experiments and evaluated the final version of the manuscript.

Signed Date 22/10/15

Andrew J. Cole
I cultivated biomass for the experiments and evaluated the final version of the manuscript.

Signed Date 22/10/15

Peter J. Ashman
I supervised the development of work and evaluated the final version of the manuscript.

Signed Date 16/10/15

Biomass and Bioenergy 83 (2015) 183–195

Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: http://www.elsevier.com/locate/biombioe

Research paper

Mobilisation of trace elements during thermal conversion of algae cultivated in ash dam water

Daniel J. Lane [a, *], Philip J. van Eyk [a], Rocky de Nys [b], David A. Roberts [b], Andrew J. Cole [b], Peter J. Ashman [a]

[a] School of Chemical Engineering, The University of Adelaide, Adelaide, SA 5005, Australia
[b] MACRO – the Centre for Macroalgal Resources and Biotechnology, College of Marine and Environmental Sciences, James Cook University, Townsville, Qld 4811, Australia

ARTICLE INFO

Article history:
Received 21 May 2015
Received in revised form
11 September 2015
Accepted 25 September 2015
Available online xxx

Keywords:
Algal biomass
Thermal conversion
Trace elements
Volatilisation
Leaching

ABSTRACT

The work presented here assesses the potential for the mobilisation of 11 trace elements (As, Be, Co, Cu, Mn, Ni, Pb, Sb, Se, V, Zn) during the thermal conversion of micro- and macroalgae that were cultivated in ash dam water. The volatility of the trace elements was quantified by mass balances based on elemental analyses of char and ash residues. The residues were prepared in a laboratory-scale fixed-bed reactor at a range of different temperatures (500–1100 °C) and gas atmospheres (N_2, 2% O_2 and CO_2) to simulate pyrolysis, combustion and gasification processes. The results showed high volatilities for Se (~79–97%) and As (~51–79%) below 500 °C. Zn, Pb and Sb were mainly volatilised above 700 °C. The different gas atmospheres had little influence on the volatility of these elements, which increased sharply to more than 90% with increasing temperature from 700 to 1100 °C. Volatilities for V, Mn, Cu, Co, Ni and Be were relatively minor over the full range of investigated operating conditions. Samples of each alga and their thermal conversion residues were subject to batch leaching in water. All of the tested trace elements, except for Pb and Be, were partially leached from the algae. Vanadium was up to 4–5 times more leachable in the combustion residues than in the algae. The other trace elements were generally less leachable following thermal conversion. The trace elements were more stable in residues prepared under pyrolysis and gasification conditions than in residues prepared under combustion conditions at the same temperature.

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1. Introduction

Vast volumes of waste water are generated at coal-fired power stations, particularly in countries like Australia where it is common practice to dispose of coal-ash in large ponds, known as ash dams. Ash dam water (ADW) often contains potentially harmful trace elements (TEs), which have been leached out of coal-ash, in concentrations that exceed water quality criteria [1]. In such cases the ADW cannot be safely discharged from the power station. Cost effective and environmentally sustainable technologies are critical to remediate ADW and render it reusable. A new technology being developed at the Centre for Macroalgal Resources and Biotechnology at James Cook University involves the integrated production of algae in ADW to sequester environmentally important TEs. Recent studies [1,2] have demonstrated the production of algae in TE contaminated ADW from the Tarong power station in Queensland, Australia. The concentrations of most regulated TEs in the ADW were successfully reduced to levels that comply with Australian water quality standards [3]. However, effective utilisation of the produced algal biomass still remains a key challenge for the algal-based bioremediation concept.

Thermal conversion, by means of pyrolysis, combustion or gasification, is one possible use of the produced ADW algae that allows for heat and power generation. Much of the infrastructure required for heat and power generation is likely already available at the power station and the total volume of bio-solids is substantially reduced in the process which is beneficial from the point of waste management. However, there are potential risks in the case that the TEs sequestered by the algae become mobile. If released into the environment the TEs can accumulate at levels much higher than which they occur naturally [4] and cause significant harm to

* Corresponding author.
E-mail address: daniel.lane@adelaide.edu.au (D.J. Lane).

http://dx.doi.org/10.1016/j.biombioe.2015.09.013
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delicate ecosystems and to human health [5,6]. The different pathways for the TEs to make their way into the environment are shown schematically in Fig. 1. The TEs are introduced to the power station with the coal feed which is combusted in a boiler at high temperatures to produce heat and power for electricity generation. Bottom ash and fly ash are generated as by-products during this process. The fly ash is generally enriched in various TEs and is disposed of in an ash dam. The algae can be used to remediate the ADW in bioremediation ponds by sequestering TEs dissolved in the water via a two-phase process [7]. The first phase involves passive adsorption of the TE onto cell surfaces and the second phase involves transport of the TE across the cell wall and into the cytoplasm, where it can be stored in a non-toxic form [8]. The produced algae is harvested, dried and then used as a feedstock for thermal conversion (*i.e.* pyrolysis, combustion or gasification). During thermal conversion, the TEs can be released into the gas phase or be retained in the solid ash (or char) residues. Volatilised TEs risk being emitted from the stack and into the atmosphere. The TEs retained in the solid residues can undergo further fractionation if the residues are contacted with water. TEs leached from the residues can migrate to and contaminate ground and surface waters [9]. Roberts *et al.* studied the potential for TE leaching from ADW algal chars produced under slow pyrolysis conditions [2] and the transfer of TEs from the produced chars to edible crops and soil pore water [10]. Apart from this work, little has been done to assess the potential for TE mobilisation both during and post thermal conversion of ADW algae, particularly under conditions relevant to industrial heat and power applications.

The volatility of the TEs during thermal conversion has been studied for coal and for terrestrial biomass fuels by means of thermodynamic equilibrium calculations (TECs) [11–13], laboratory scale experiments [14,15] and ash sampling at full scale plants [16,17]. The ranges of volatilities reported in these studies vary widely for many of the TEs. Nevertheless some general trends are evident. Selenium is predominately volatilised at low temperatures (<500 °C), regardless of the gas atmosphere. As, Pb, Sb and Zn display intermediate volatilities. The volatility of these elements is highly sensitive to temperature and tends to be greater under reducing gas atmospheres which are characteristic of gasification and pyrolysis processes. Co, Mn, Ni and V are more or less refractory below 1100 °C or are volatilised only to a minor extent. Studies that address the volatility of Cu are particularly conflicting. Some studies [18,19] report Cu to be mainly retained in the char and ash residues at temperatures below 1100 °C. Other studies [13,14] indicate that Cu is largely volatilised below 1100 °C. Available literature on the volatile behaviour of Be is limited [11,20]. Several authors [12,21,22] have emphasised that the extent of TE volatilisation depends on both fuel composition and on operating parameters such as temperature and gas atmosphere. The chemical composition of algae has been studied in previous work [23,24] and was found to differ in many ways from that of coal and commonly used terrestrial biomass fuels. Despite this, there has been limited work to determine the extent to which the TEs are volatilised from algae during thermal conversion or to understand how this varies for different temperatures and for different gas atmospheres.

A large amount of research has been dedicated to understanding the leaching behaviour of the TEs in terrestrial fuels and in their char and ash residues. In general, the extent of TE leaching from the char and ash residues cannot be correlated with the leachable fraction in the original feedstock [25]. The leachability of a TE depends on its chemical form (particularly oxidation state) [25–27] and on its spatial distribution in the fuel or residue [27]. Both of these properties can be altered during thermal conversion depending on the operating conditions. Formation of oxides, hydroxides and sulphates of the TEs are common under combustion conditions whereas reduced species tend to be formed under gasification conditions [11]. Certain TEs, especially those which volatilise and re-condense during thermal conversion (*e.g.* As, Sb, Se and Zn), can become enriched on char and ash particle surfaces [27] where they are more susceptible to leaching. The leachability of the TEs following thermal conversion is not only affected by the transformations of the TEs themselves but also by the transformations of the major and minor inorganic elements (*e.g.* Ca and S). The behaviour of the major and minor inorganic elements in the char and ash residues largely controls the pH of the leachate produced when the residue is brought into contact with water [28].

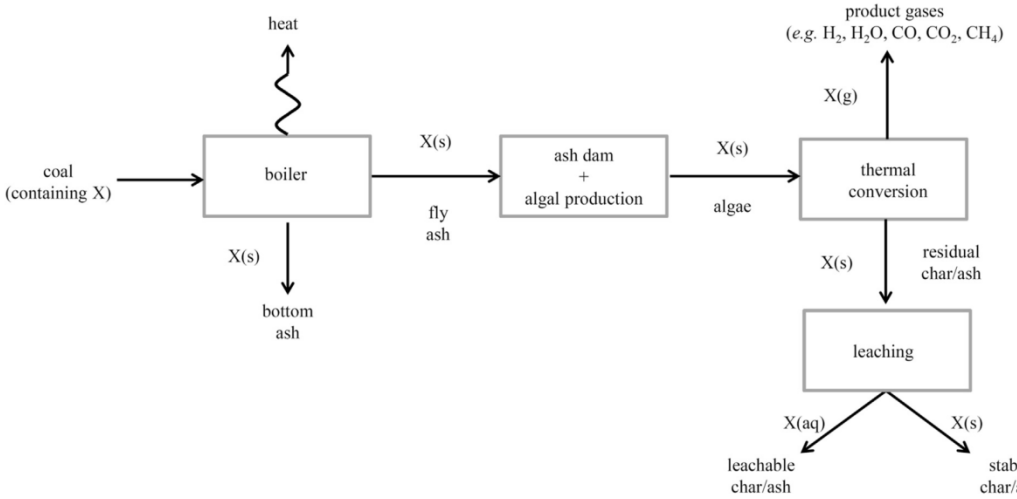

Fig. 1. Trace element flows and processes in the concept for combined algal bioremediation and thermal conversion. Trace element flows are indicated by the letter "X". The phase of the trace elements (*e.g.* solid, gas, aqueous) is indicated inside parentheses to the right of the letter "X".

The leachate pH is known to play key a role in controlling the extent of initial dissolution of the TEs as well as the precipitation of secondary phases which collectively control the overall solubility of the TEs [26–28]. Literature which deals with TE leaching from algal biomass and their char and ash residues is limited. Previous work [2] has shown macroalgal chars, produced under slow pyrolysis conditions, to contain a higher total TE content but lower exchangeable TE content than algal biomass. Less is known about TE leaching from algal chars produced under fast pyrolysis conditions or from algal ashes produced under combustion and gasification conditions and how the leaching behaviour of these residues compares to that of the algal feedstock itself.

This paper investigates the potential for the mobilisation of 11 environmentally important TEs (As, Be, Co, Cu, Mn, Ni, Pb, Sb, Se, V and Zn) during the thermal conversion of ADW algae. The first aim of this paper was to determine the volatility of the TEs as a function of thermal conversion temperature (500–1100 °C) in gas atmospheres relevant to pyrolysis, combustion and gasification processes. The second aim was to provide a preliminary assessment of the leachability of the TEs in the ADW algae and in char and ash residues prepared under different gas atmospheres and at different temperatures.

2. Materials and methods

2.1. Algal samples

Two samples of algae were used in this work; a species of macroalgae from the genus *Oedogonium* (Genbank KF606974) [29] and an artificially mixed polyculture of microalgae which is dominated by the species *Schroederiella apiculate* and *Scenedesmus dimorphus* [30]. Both samples are key targets for the remediation of industrial waste waters [1,31]. The samples produced for this work were both grown directly in ADW at the Tarong power station (700 MW) in Queensland, Australia (26°46′51″S, 151°54′45″E). The Tarong ash dam is used to dispose of fly ash produced during coal combustion. It has a capacity of approximately 46 GL. The *Oedogonium* biomass (hereafter referred to as "OD") was cultured in May 2013 and was harvested by filtration followed by centrifugation. The polyculture of microalgae (hereafter referred to as "TPC") was cultured in June 2013 and was harvested by centrifugation. Detailed descriptions of the growth and harvesting methods can be found in previous work by Roberts *et al.* [2] and Lane *et al.* [24] for OD and TPC respectively.

Harvested algal samples were air-dried until the moisture contents of the algae were in equilibrium with the moisture in the atmosphere. Representative samples of the dried algae were milled in a centrifugal knife mill and then sieved to obtain the 1.6–6.4 mm size fraction. This size fraction was used to produce char and ash samples. Samples of each alga were also milled to pass through a 250 μm screen. This smaller size fraction was used for fuel analyses. The proximate compositions and the elemental concentrations of the major and minor elements are presented in Table 1 for the two ADW algae. Moisture contents were determined by oven-drying at 105 °C. Volatile matter, fixed carbon and ash contents were determined by means of thermogravimetry [24]. The high ash contents in OD (20.9% w/w, dry basis) and TPC (23.1% w/w, dry basis) can be attributed to the high levels of major and minor inorganic elements (>0.1% w/w) in the ash dam water growth medium.

2.2. Preparation of char and ash residues

Char and ash residues were prepared in a laboratory-scale, fixed bed reactor, at temperatures between 500 and 1100 °C, using the ADW algae as feedstocks. Three gas atmospheres, N_2, 2% O_2/bal. N_2 and CO_2, were used to simulate pyrolysis, combustion and gasification processes. The residues were weighed at the end of each test and analysed to determine the concentrations of the TEs in the residues. The extent of TE volatilisation from the ADW algae was then calculated by mass balance according to Eq. (1):

Table 1
Proximate compositions and major and minor element concentrations for the two ADW algae. All data has been taken from Lane *et al.* [24].

Algae:	OD	TPC
Proximate composition (% w/w)		
moisture[a]	7.3	10.8
volatile matter[b]	58.7	57.7
fixed carbon[b]	20.4	19.0
ash[b]	20.9	23.3
Elemental composition (% w/w)[b]		
C	34.8	41.3
H	5.0	5.8
N	5.4	6.9
S	0.53	1.01
Cl	0.25	0.50
P	1.37	1.36
Na	0.23	0.51
K	1.08	0.59
Ca	1.00	1.67
Mg	0.26	0.34
Si	7.55	6.99
Fe	1.60	0.44
Al	0.35	0.21
Ti	0.0102	0.0062

[a] After drying.
[b] Dry basis.

$$\%\ volatilised = \left[1 - \frac{1}{(1-M)}\left(\frac{W_r}{W_A}\right)\left(\frac{C_{r,i}}{C_{A,i}}\right)\right] \times 100 \qquad \text{Eq. 1}$$

Where M is the moisture fraction of the algal feedstock (w/w), W_r and W_A are the weights (mg) of the residue and corresponding algal feedstock respectively, and $C_{r,i}$ and $C_{A,i}$ the concentrations (w/w, dry basis) of element i in the residue and feedstock respectively.

A detailed description of the reactor setup and its operation has been reported previously [24], but a brief summary is provided here. A loaded sample boat, containing 1–4 g of ADW algae (weighed to the nearest 0.1 mg), was inserted into a preheated reactor. For pyrolysis tests, N_2 was fed to the reactor at a rate of 4.0 L min^{-1} @ STP. For combustion and gasification tests, samples were first pyrolysed in N_2 before switching the gas atmosphere over to 2% O_2/bal. N_2 (combustion) or to CO_2 (gasification). Pyrolysis, combustion and gasification reactions were allowed to proceed until completion. Reaction progress was monitored by measuring the concentrations of CO and CO_2 in the product gases. At the end of each test the gas atmosphere was switched to N_2, the heating elements turned off and the sample boat retracted to the cool zone of the reactor. Once the temperature of the sample boat dropped to below 50 °C the ash (or char) residue was removed from the furnace and weighed immediately. The residue was then ground to a fine powder using a mortar and pestle and then stored in an air-tight, plastic container for analysis.

2.3. Trace element leaching

The ADW algae and their pyrolysis, combustion and gasification residues were leached in deionised (DI) water in order to assess the solubility of the TEs. The tested residues included combustion ashes prepared at various temperatures between 500 and 1100 °C as well as pyrolysis chars and gasification ashes prepared at 1000 °C.

Samples (100 mg) were mixed with DI water (4.0 g) in polyethylene centrifuge tubes (15 ml) and then shaken on a rotary shaker for 24 h at room temperature. Leached samples were then centrifuged (3750 rpm, 5 min) and the supernatants filtered through 0.2 μm, polyvinylidene fluoride syringe filters. The solid residues were then subject to a second water extraction in another 4.0 g of deionised water. The two extracts were combined and the pH of the resultant solution measured. The combined extract was then acidified using concentrated HNO_3 (68% v/v) so that the final concentration of HNO_3 in the extract was 5% v/v. All plasticware used in the leaching tests was cleaned before use by soaking in a 3 M solution of HCl for a period of 12 h. For quality assurance, select samples were leached in triplicate and a blank was analysed in addition to the unknown samples.

2.4. Chemical analysis

TE concentrations were determined using solution-based inductively coupled plasma mass-spectrometry (ICP-MS). Solid samples were first digested in $H_2O_2/HNO_3/HF$ using a procedure described by Lane *et al.* [24]. All samples were diluted in HNO_3 (5% v/v) using acid (3 M HCl) cleaned plasticware so that the resultant TE concentrations were within the linear calibration range (10–500 ppb) of the ICP-MS instrument. For most samples, three different levels of dilution were needed to measure all of the studied TEs accurately. Solution analysis was done at Adelaide Microscopy, The University of Adelaide, using an Agilent 7500ce instrument (Agilent Technologies, Tokyo, Japan). Element isotopes without known spectral interferences were preferentially selected for analysis. An octopole reaction system (ORS) was used to remove polyatomic interferences for TEs which do not have abundant, interference-free isotopes. The ORS was operated in collision mode, using pure He as the cell gas (4.5 ml/min @ STP). The ORS separates interfering polyatomic ions from the relatively small analyte ions based on differences in ion size. For sample introduction the ICP-MS was equipped with a Miramist nebulizer and a quartz spray chamber, into which samples were introduced by a peristaltic pump at a flow rate of 1.0 mL min^{-1}. An internal standard, Indium, was mixed online with the samples to compensate for matrix effects and instrument drift. All element concentrations were determined against certified multi-element calibration standards (Choice Analytical, Australia) and blanks were interspersed throughout the analysis session. The linearity of the calibration curves was evaluated by computing R^2 values. The R^2 values were all greater than 0.997. The instrument was operated with an RF power of 1.5 kW, a carrier gas flow of 0.89 L min^{-1} and a make-up gas flow of 0.19 L min^{-1}. The sample uptake rate was 1.0 mL min^{-1} and the dwell times were set to 20 ms. Three replicates were obtained for each sample. The data was processed using Agilent MassHunter Data Analysis™.

For each batch of analysis at least one blank and a certified reference material, BCR-2 (U.S. Geological Survey, USA) [32], were analysed in addition to the unknown samples. BCR-2 is a sample of powdered basalt from the Bridal Veil Flow Quarry, Washington. The char and ash samples were analysed once for TE concentrations. The algal samples, OD and TPC, were analysed in triplicate in order to estimate the error in the measurement of the TEs. Relative standard deviations of the TE concentrations were all within 9%.

3. Results and discussion

The concentrations of select TEs are presented in Table 2 for the two ADW algae (OD and TPC). The values vary widely for the different TEs, ranging from just above 1 ppm to 893 ppm. TE concentrations commonly reported for coal [22] have also been included in Table 2 for comparison. The values for some of the TEs, namely Se, As and V, are much greater in the ADW algae than in most coals. These elements are largely sequestered by the algae during cultivation [1,2] and are given special attention in the proceeding discussion.

Table 2
Concentrations of 11 trace elements in the ADW algae, OD and TPC. All data are reported as average concentrations (mg kg^{-1}, dry basis) ± 1 S E. (n = 3). Data for the algal samples are compared to trace element concentrations commonly reported in coal.

Concentration (mg kg^{-1}, dry basis)			
Element	OD	TPC	Coal [22]
As	104 ± 2	21.9 ± 0.5	0.5–10
Be	11.4 ± 0.8	3.16 ± 0.1	0.1–10
Co	6.12 ± 0.08	1.35 ± 0.03	0.5–20
Cu	61.7 ± 0.6	16.5 ± 0.4	5–60
Mn	875 ± 9	61.0 ± 3	5–300
Ni	50.5 ± 0.7	48.3 ± 5	0.5–100
Pb	1.75 ± 0.4	1.73 ± 0.03	1–300
Sb	4.19 ± 0.07	2.79 ± 0.03	<1
Se	8.46 ± 0.2	27.9 ± 0.9	0.2–3
V	893 ± 5	270 ± 8	1–100
Zn	434 ± 20	473 ± 20	1–1000

3.1. Trace element volatility

TE volatility profiles are presented in Fig. 2 for Se and As, in Fig. 3 for Zn, Pb and Sb, and in Fig. 4 for V, Mn and Cu. Volatility profiles for Be, Co and Ni are similar to those of V, Mn and Cu and can be found in Figure A1. The volatility profiles show the extent to which the TEs are volatilised as a function of temperature for the two ADW algae, under gas atmospheres (N_2, 2% O_2/bal. N_2 and CO_2) relevant to pyrolysis, combustion and gasification processes. Note that data is not shown for CO_2 gasification at 500 °C since the algal chars were barely reactive at this condition. The volatile behaviour of the TEs can be categorised into three different types. Type 1 TEs (see Fig. 2) are highly volatile. Over 50% of the TE is volatilised below 500 °C and 90–100% is volatilised by 1100 °C. Se and As are both Type 1 TEs. Type 2 TEs (see Fig. 3) have intermediate volatilities. These elements have relatively low volatilities below 700 °C however are substantially volatilised between 700 and 1100 °C. Type 2 TEs include Zn, Pb and Sb. Type 3 TEs have low volatilities below 1100 °C and become enriched in the char and ash residues at all temperatures. Be, Co, Cu, Mn, Ni and V are all Type 3 TEs.

In order to estimate the accuracy of the reported volatility values select tests were repeated. Combustion of OD at 500 °C was performed in triplicate. The following tests were performed in duplicate: pyrolysis of OD at 500 °C, pyrolysis of OD at 700 °C and gasification of OD at 850 °C. Errors in the volatility values (95% confidence interval) are within 10% for all of the trace elements except for Pb which has an error of 16%. Errors in the volatility values diminish with increasing extent of volatilisation and are in general lower for TEs with concentrations in the algae greater than 10 ppm.

3.1.1. Type 1 TEs (highly volatile)

Over 75% of the Se in OD and 95% of the Se in TPC is volatilised by 500 °C in all three of the tested gas atmospheres (see Fig. 2). The remaining Se in OD is more or less completely volatilised by 850 °C under combustion and gasification conditions. Under pyrolysis conditions, a small amount of the total Se in OD (10–20%) is retained in the char residue. This finding contradicts established work by Frandsen *et al.* [11] who used thermodynamic equilibrium calculations (TECs) to predict the volatilisation of Se during the

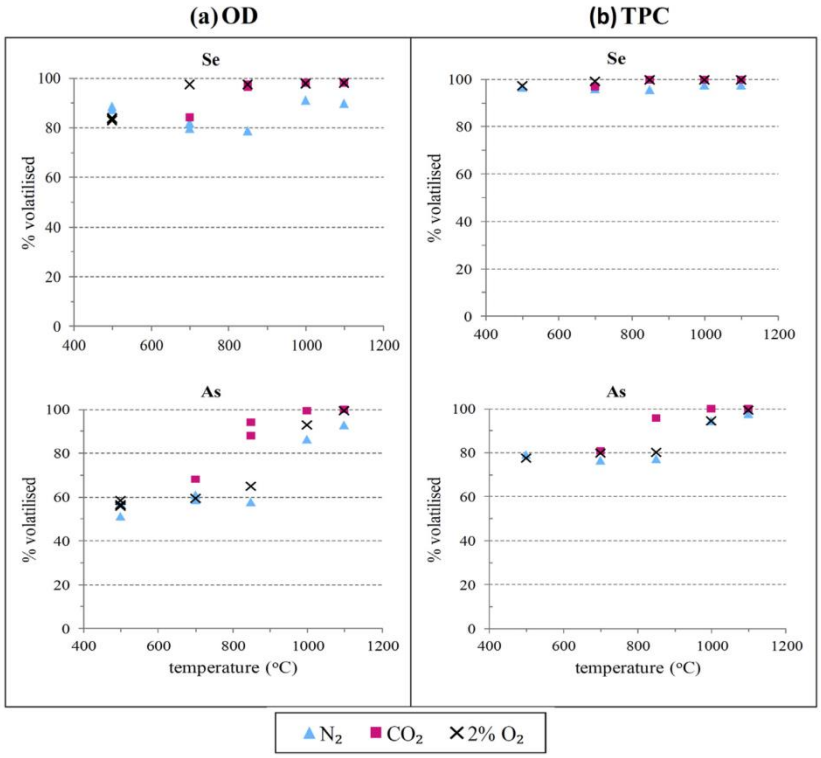

Fig. 2. Volatilisation of Se (top) and As (bottom) from OD (a) and TPC (b) as a function of reactor temperature. Data are presented for pyrolysis (N_2), combustion (2% O_2/bal. N_2) and gasification (CO_2) gas atmospheres. Note that data is not shown for CO_2 at 500 °C.

thermal conversion of coal. Their calculations showed Se to be completely volatilised from coal by 200 °C. Changes in gas atmosphere were found to affect only the distribution of Se-containing species in the gas phase at temperatures above 500 °C but not the partitioning of Se between the gas phase and condensed phases. It is noted that TECs assume chemical equilibria and therefore do not take into account kinetic and mass transport limitations during thermal conversion. It is possible that the Se in OD is partially present in a form that is not accessed during pyrolysis and that the volatilisation of Se is mass transport limited. This may account for the discrepancy between the two studies. In a more recent study, Liu *et al.* [33] measured the volatilisation of Se during coal gasification and partitioned the release of Se between initial pyrolysis and gasification of the residual char. Their reported partitioning indicates that part of the Se in coal is retained in the char during pyrolysis and is later released during the gasification phase of fuel particle burnout. The work of Liu *et al.* [33] and the observed behaviour of Se in OD could imply that for some fuels, including OD, either an oxidising or reducing furnace atmosphere, which are characteristic of combustion and gasification processes, is required to completely volatilise Se.

Around 50% of the As in OD and around 75% of the As in TPC is volatilised by 500 °C (see Fig. 2). The remaining As is almost completely volatilised by 1100 °C. The extent of volatilisation of As is greater under gasification conditions than under pyrolysis and combustion conditions, particularly within the temperature interval 700–1100 °C. This finding is consistent with trends reported in the literature for coal [11] and for terrestrial biomass fuels [12]. Various authors [12,34] have attributed the reduced volatility of As under oxidising conditions to the capture of gas phase As by Ca in the ashes, according to the following heterogeneous reaction [35]:

$$As_2O_3(g) + O_2(g) + 3CaO \leftrightarrow Ca_3(AsO_4)_2(s) \quad \text{Eq. 2}$$

The formation of calcium arsenate in the above reaction requires oxygen to be present in the gas phase and is therefore favoured by oxidising (combustion) conditions. Under oxidising conditions calcium arsenate is stable in the condensed phase at temperatures as high as 1000 °C [12]. A similar phenomenon likely accounts for the differences in the volatile behaviour of As in the ADW algae under the different gas atmospheres given the high levels of Ca in OD (1.0% w/w, dry basis) and TPC (1.7% w/w, dry basis).

The volatile behaviour of As has been studied extensively with respect to combustion of chromated copper arsenate (CCA) impregnated wood [19,36]. A greater proportion of the total As is volatilised from ADW algae than from CCA impregnated wood, particularly at low temperatures (<500 °C). Less than 35% of the total As is volatilised from CCA impregnated wood during combustion at 500 °C [19,36], compared with ~51–89% from the ADW algae. The greater volatility of As in the ADW algae may be due to differences in the absolute amount of As in the two fuels. There are typically 1–2 orders of magnitude more As in CCA impregnated wood than in the ADW algae.

3.1.2. *Type 2 TEs (intermediate volatilities)*

Zinc is mainly volatilised from the ADW algae within the

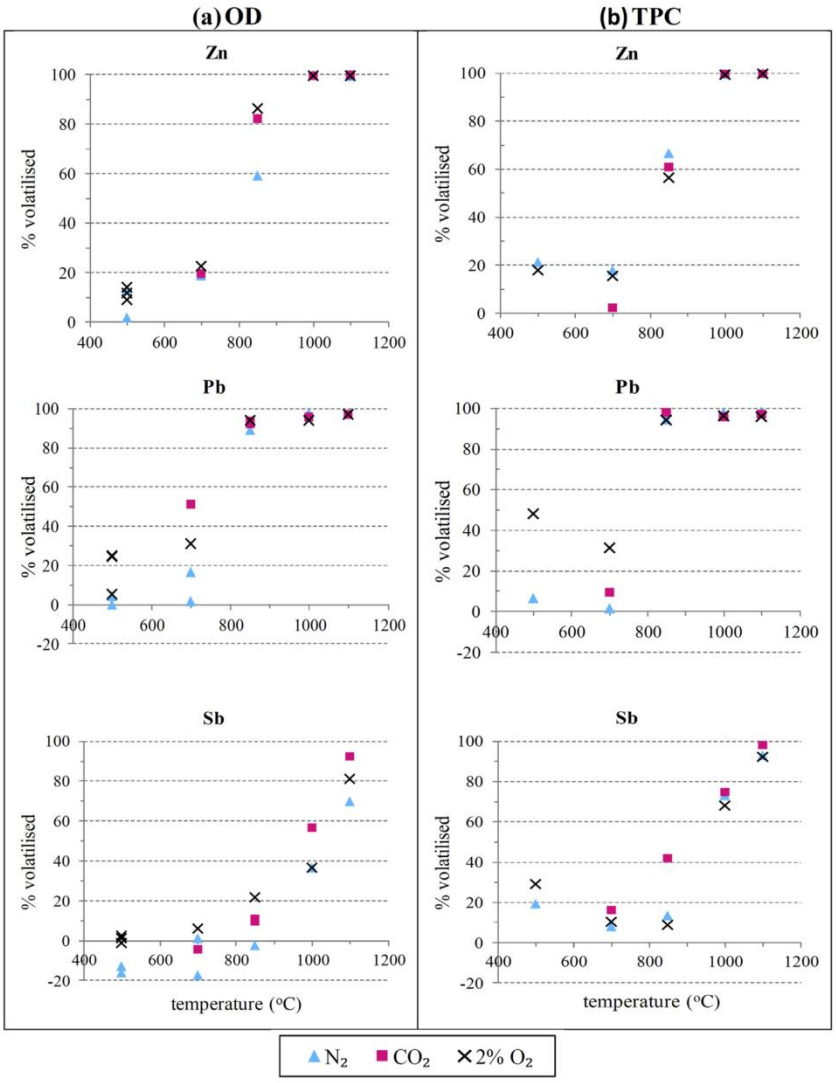

Fig. 3. Volatilisation of Zn (top), Pb (middle) and Sb (bottom) from OD (a) and TPC (b) as a function of reactor temperature. Data are presented for pyrolysis (N_2), combustion (2% O_2/bal. N_2) and gasification (CO_2) gas atmospheres. Note that data is not shown for CO_2 at 500 °C.

temperature interval 700–1000 °C (see Fig. 3). Only low levels of Zn (<25%) are volatilised below 700 °C. Differences in the furnace gas atmosphere have only a minor influence on the volatility of Zn. The volatile behaviour of Zn in terrestrial fuels has been studied extensively using TECs [11,12,21,37]. These studies all predict the local gas atmosphere to have a significant influence on the volatility of Zn. Under reducing conditions Zn is readily volatilised below 900 °C whereas under oxidising conditions zinc is thought to be largely retained in the form of oxides up until approximately 1000 °C [11,12,21]. The similarity in the volatile behaviour of Zn under the three different gas atmospheres (N_2, 2% O_2 and CO_2), within the temperature interval 700–1000 °C, suggests that the local gas atmosphere inside the algae particles is sufficiently reducing during pyrolysis to inhibit the retention of Zn as oxides. During pyrolysis, loosely bound organic matter is released rapidly from the fuel matrix in the form of volatile gases (*e.g.* CO, CO_2, H_2O, H_2, CH_4). This can have the effect of temporarily creating a reducing atmosphere inside and at the surface of the burning fuel particles. It is therefore possible that Zn is volatilised in a reducing atmosphere in pyrolysis and combustion processes despite the global furnace atmosphere being inert or oxidising. The high levels of Cl in OD (0.25% w/w, dry basis) and TPC (0.50% w/w, dry basis) may also aid the volatilisation of Zn at low temperatures [12,38].

Lead is slightly more volatile than Zn (see Fig. 3) however the overall trends for Pb are similar to those observed for Zn. Previous laboratory-scale, experiments on the combustion of wood and wood-derived fuels [14,15] showed similar volatilities for Pb. Measurements at full-scale plants indicate slightly lower volatilities

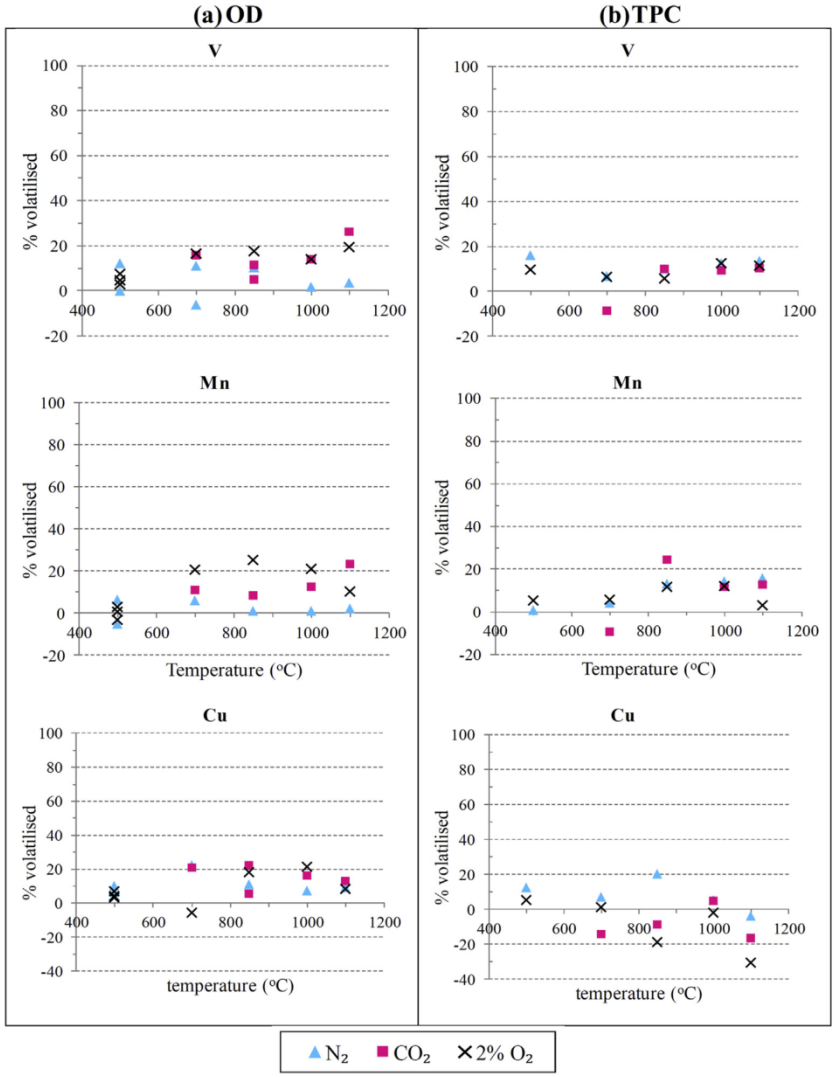

Fig. 4. Volatilisation of V (top), Mn (middle) and Cu (bottom) from OD (a) and TPC (b) as a function of reactor temperature. Data are presented for pyrolysis (N_2), combustion (2% O_2/bal. N_2) and gasification (CO_2) gas atmospheres. Note that data is not shown for CO_2 at 500 °C.

for Pb. Wilde and Halbrook [20] reported 63% of the Pb in coal to be volatilised at 1000 °C in the char-oil-energy development (COED) gasification process. Brunner and Mönch [16] found over half of the total Pb in municipal solid waste to report to the slag phase in an industrial scale incinerator operating at 900 °C.

Antimony is mainly volatilised from the ADW algae above 850 °C (see Fig. 3). By 1100 °C 70–100% of the total Sb in the ADW algae is volatilised. The slightly negative volatility values reported for OD within the temperature interval 500–850 °C are likely due to inhomogenities in fuel composition but may also have been caused by errors in the measurement of Sb. As with Zn and Pb, the gas atmosphere appears to have only a minor influence on the volatility of Sb.

3.1.3. Type 3 TEs (low volatilities)

Be, Co, Cu, Mn, Ni and V mainly remain in the char and ash residues below 1100 °C, in all of the tested gas atmospheres. The results for Co, Ni, Mn and V agree well with trends reported for terrestrial fuels. These elements are generally reported as being refractory during thermal conversion [11,13,39]. They may volatilise below 1100 °C in the presence of HCl(g), but only to a minor extent [13]. A wide range of volatilities have been reported in the literature for Cu. Measurements at full-scale waste incinerators [16,17] show 89–96% retention of Cu in bottom ash and slag. Less than 1% of the Cu in CCA impregnated wood was found to volatilise during combustion at 1000 °C in an experimental study by Lundholm *et al.* [19]. Bunt and Waanders [18] predicted no more than 10% of the Cu in

coal to volatilise below 1100 °C during gasification in a Sasol-Lurgi gasifier. Other studies indicate that Cu is volatilised to a much greater extent. Miller *et al.* [14] reported more than half of the Cu in wood-bark to volatilise by 800 °C in a laboratory-scale reactor. Verhulst *et al.* [13] modelled the volatilisation of Cu during waste incineration. Their model showed only gas phase species of Cu to be stable above 1000 °C. Quantitative literature on the volatility of Be is scarce. Wilde and Handbrook [20] reported 18% of the total Be in coal to volatilise at 1000 °C in the COED gasification process. On the other hand, Frandsen *et al.* [11] predicted complete volatilisation of Be by 1000 °C during the combustion of coal, based on TECs.

3.2. Trace element leachability

Water leaching results are presented in Fig. 5 for Se and As, in Fig. 6 for Zn, Pb and Sb and in Fig. 7 for V, Mn and Cu. Results for Co, Ni and Be can be found in Figure A2. These figures show the water extractable fraction and the total concentration of the TEs in the algae and combustion ash samples and how these values vary for different combustion temperatures. Results are all expressed as mg per kg of dry algae. TE volatilisation is indicated by a reduction in the total TE concentration with increasing combustion temperature. The pH values of the ash leachates are presented in Fig. 8a as a function of combustion temperature. The values range between pH 5.0 and 7.7. The ash leachates become increasingly acidic with increasing combustion temperature from 500 to 1100 °C.

Approximately one-third of the total Se and 38–65% of the total As in the ADW algae is water extractable. Combustion of the ADW algae results in a significant reduction in the leachability of both Se and As. For Se, the water extractable fraction in the combustion ashes is well below the limit for accurate detection (<0.2 mg kg^{-1} of dry algae). For As, the water extractable fraction is reduced to below 14% during combustion. At high combustion temperatures (>1000 °C) the amount of water extractable As becomes negligible.

Zinc is partially water extractable (4–9%) in the ADW algae but is not extractable in the ashes. Lead is more or less insoluble in both the ADW algae and in their ashes. Approximately 50% of the Sb in the ADW algae is water extractable. Antimony is less leachable in the combustion ashes. The combustion temperature has a clear effect on the leachability of Sb in the ashes however its effect is not consistent for the two samples of alga. In the case of OD, Sb is virtually insoluble in the ashes prepared at 500 and 700 °C however is partially leachable (15–25%) in the ashes prepared at 850, 1000 and 1100 °C. In the case of TPC, Sb is partially leachable (16–29%) in the ashes prepared at 500, 850 and 1000 °C but is not leachable in the ashes prepared at 700 and 1100 °C. There is no clear relationship between the leachability of Sb in the ashes (Fig. 6) and the pH of the corresponding water extracts (Fig. 8a).

Vanadium is partially water extractable (12–26%) in the two ADW algae. Interestingly, the leachability of V is, in general, greater in the ashes than in the corresponding algal feedstocks. The TPC combustion ashes prepared at 1100 °C is an exception to this trend.

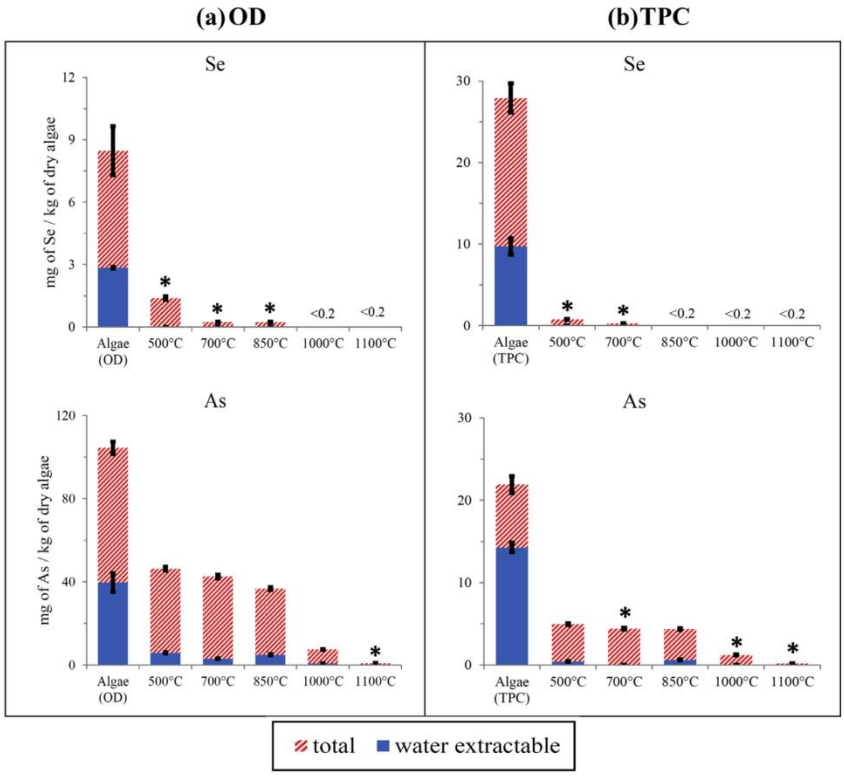

Fig. 5. Leachability of Se (top) and As (bottom) in ADW algae and in combustion ashes prepared at various temperatures. Results are presented for OD (a) and TPC (b). All data are expressed as mg kg^{-1} of dry algae ± 2 S E. An asterisk (*) is used to indicate where the water extractable concentration is below the limit for accurate detection (0.2 mg kg^{-1}). Differences in the y-axis scales for OD and TPC account for the different concentrations of As and Se in the two algae.

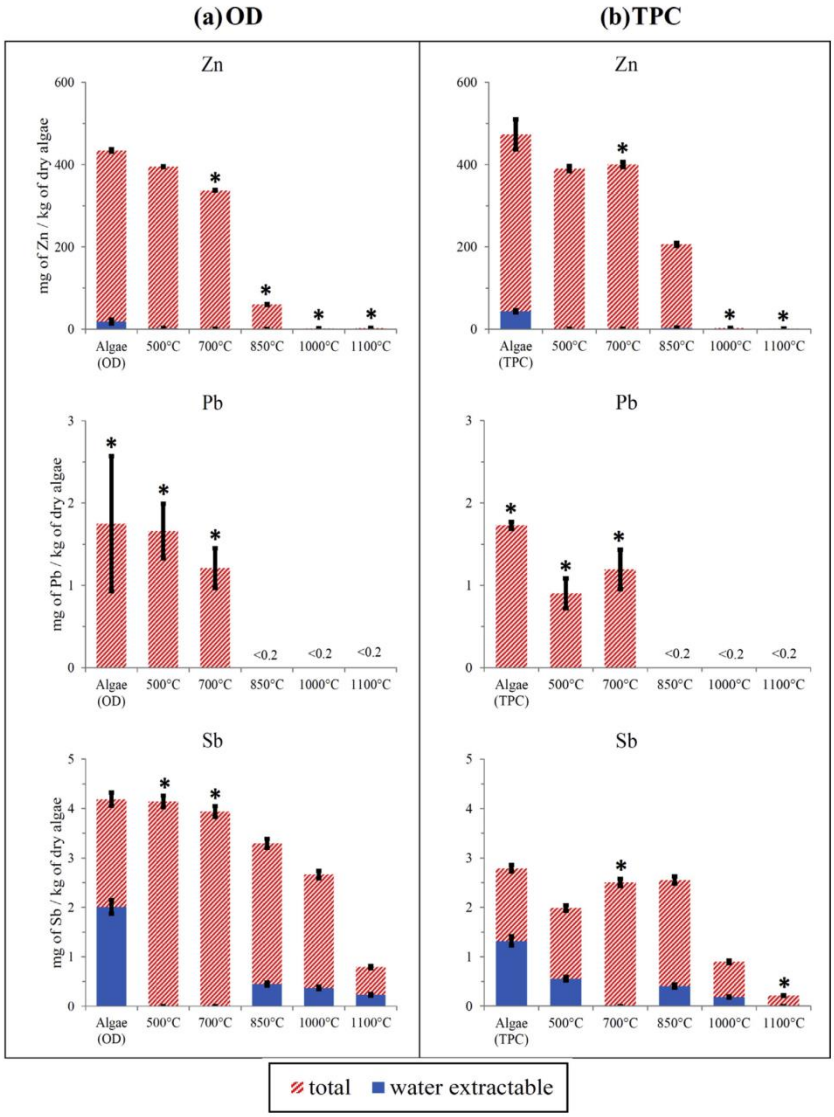

Fig. 6. Leachability of Zn (top), Pb (middle) and Sb (bottom) in ADW algae and in combustion ashes prepared at various temperatures. Results are presented for OD (a) and TPC (b). All data are expressed as mg kg^{-1} of dry algae ± 2 S E. An asterisk (*) is used to indicate where the water extractable concentration is below the limit for accurate detection (0.2 mg kg^{-1}).

In this ash sample only 10% of the total V is water extractable. The leachability of V in the ashes is influenced by the combustion temperature. Vanadium is most extractable (56–57%) in the ashes prepared at 700 °C. According to Izquierdo and Querol [28], V generally becomes more soluble in coal ash with increasing pH from pH 5 to 8. In the case of the ADW algae there is no clear correlation between the leachability of V and the pH of the ash leachate. Other factors such as the speciation of V in the ashes likely control the leachability of V. Water extractable fractions of Mn Cu, Co and Ni in the ADW algae range between 15 and 20%, 14–29%, 34–36% and 36–42% respectively. Like V, the leachability of these elements in the ashes has a complex dependence on the combustion temperature. The water extractable fractions of Mn and Cu are lower in the ashes than in the corresponding algal feedstocks for all but one of the ash samples (OD ashes prepared at 1100 °C). Both Co and Ni are less leachable in all of the ash samples than in the corresponding algal feedstocks. Beryllium is practically insoluble in both the ADW algae and in their ashes.

The leaching behaviour of the TEs in the combustion ashes are compared with their leaching behaviour in the pyrolysis and gasification residues in Fig. 9. The analysed residues were all prepared at the same temperature (1000 °C) so that direct comparisons could be made between the different gas atmospheres. Note that results are not shown for Se, Zn and Pb since the concentrations of these

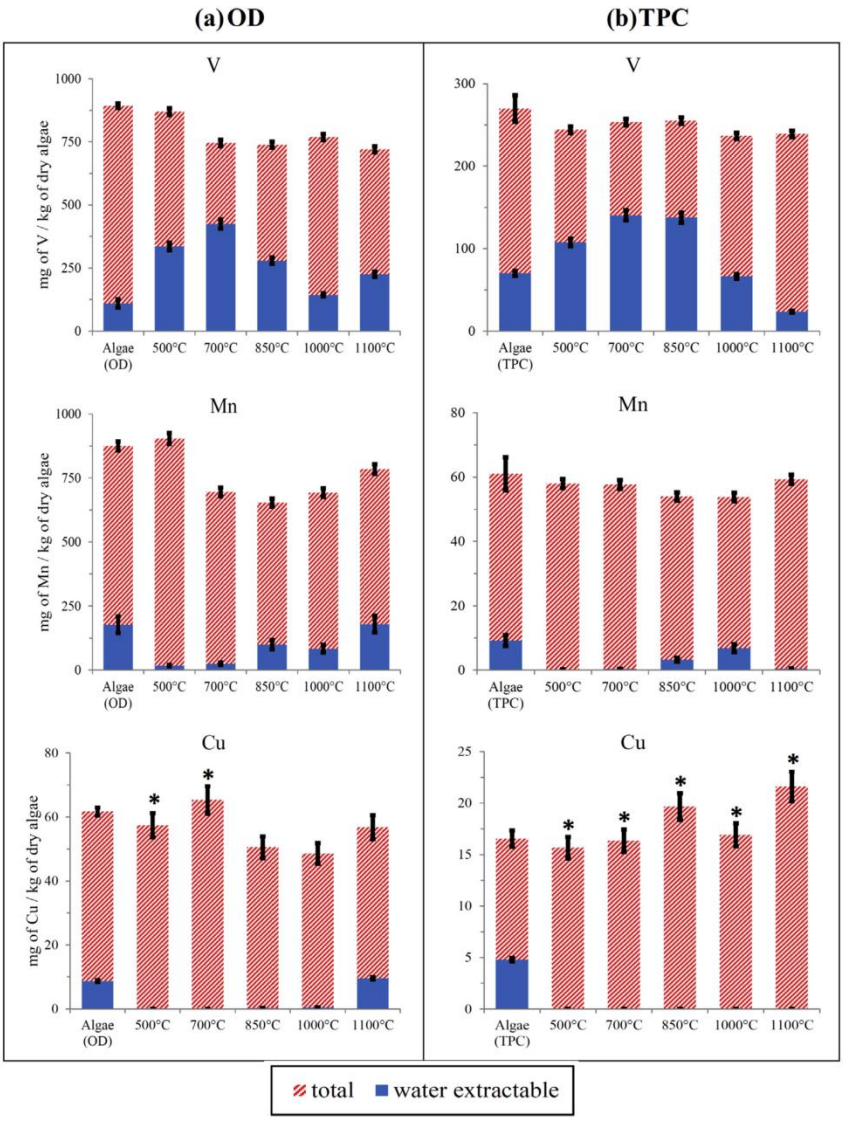

Fig. 7. Leachability of V (top), Mn (middle) and Cu (bottom) in ADW algae and in combustion ashes prepared at various temperatures. Results are presented for OD (a) and TPC (b). All data are expressed as mg kg^{-1} of dry algae ± 2 S E. An asterisk (*) is used to indicate where the water extractable concentration is below the limit for accurate detection (0.2 mg kg^{-1}). Differences in the y-axis scales for OD and TPC account for the different concentrations of the TEs in the two algae.

elements in the residues were too low (due to the volatilisation of these elements) to enable leaching analysis. Beryllium is practically insoluble in all of the residues. All other TEs are significantly more leachable in the combustion (2% O_2/bal. N_2) residues than in the pyrolysis (N_2) and gasification (CO_2) residues. The pH values of the water extracts are presented in Fig. 8b for the different types of residues. The order of acidity for the different types of residues is as follows: combustion (pH 5.0–6.2) > gasification (pH 7.4–7.8) > pyrolysis (pH 10.3–10.5). The main inorganic elements undergo different transformations during thermal conversion and form different species in the ash (or char) residues depending on the gas atmosphere [24], which affects the pH of the leachate produced when the residues are contacted with water. The leachate pH is known to play a major role in controlling the solubility of the TEs [28] and possibly accounts for the different extents of leaching from the pyrolysis, combustion and gasification residues. Leaching trends reported for coal ashes of different pH [27,28] are only in partial agreement with the results from this study. Co, Cu, Mn and Ni tend to be more leachable in slightly acidic coal ashes than in neutral or alkaline coal ashes, which is consistent with the trends observed for the ADW algae. On the other hand, As, Sb and V tend to be more leachable in neutral to slightly alkaline coal ashes (pH

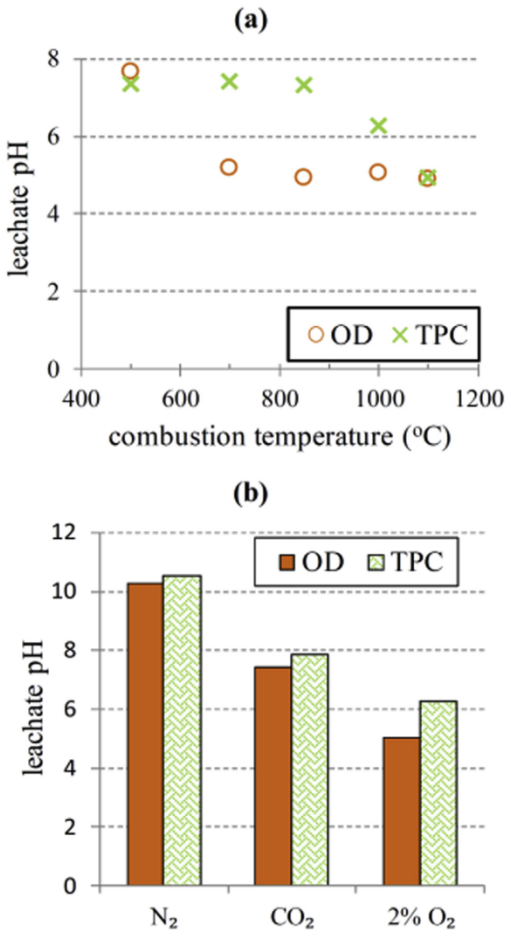

Fig. 8. pH values of water extracts from batch leaching of char and ash residues. Results are presented for combustion ashes prepared at various temperatures (a) and for residues prepared under different gas atmospheres at 1000 °C (b).

7–10.5), which is in disagreement with the trends observed for the ADW algae.

3.3. Practical implications

Several of the TEs in ADW algae volatilise during thermal conversion and may be emitted into the atmosphere. Emissions of Se and As are probably of highest concern. These two elements are associated with severe health problems [5] and there are stringent limits on their emissions from industrial processes [40]. During the thermal conversion of ADW algae, substantial amounts of both Se and As can be expected to volatilise, even under mild conditions. There are two obvious strategies for preventing emissions of Se and As. One option is to remove these elements from the ADW algae prior to thermal conversion. Washing the algae in freshwater is unlikely to be effective since both Se and As are only partially water extractable. The suitability of other methods of removal requires additional knowledge on the nature of occurrence of Se and As in the ADW algae. Another option is to capture Se and As in the product gases, post thermal conversion. Volatilised species of Se and As tend to deposit on fine particulates in the product gases or remain in the gas phase (especially Se) [22]. This makes their capture difficult with conventional flue gas cleaning systems (*e.g.* electrostatic precipitators). The use of Ca-based sorbents has been suggested for the capture of Se and As [41]. Emissions of Zn, Pb and Sb might also present problems during the thermal conversion of ADW algae, however, the volatilisation and therefore emission of these elements can largely be prevented by limiting the operating temperature to 700 °C. Such low operating temperatures may however compromise the burnout of the organic fraction.

Many of the TEs in the ADW algae, especially V, Mn, Cu, Co, Ni and Be, become enriched in the ash (or char) residues during thermal conversion. The concentration of a TE in the char or ash residue can be as much as five times higher than its concentration in the algae itself. The solid residues from the pyrolysis, combustion or gasification of ADW algae are therefore concentrated sources of several TEs. The potential for the TEs to be released from the residues has been assessed by means of batch leaching tests. Of the TEs studied, V is by far the most leachable in the char and ash residues. The environmental impact of V contamination should be further considered before utilising ADW algae as a feedstock for thermal conversion. The leachability of many of the TEs in the thermal conversion residues, including V, can be substantially reduced by operating in an inert (pyrolysis) or a reducing (gasification) gas atmosphere.

4. Conclusions

The present work assesses the mobility of 11 trace elements (As, Be, Co, Cu, Mn, Ni, Pb, Sb, Se, V, Zn) during the thermal conversion of two samples of algae that were cultivated in ash dam water. The vast majority of the Se in the algae is volatilised (~79–97%) at low temperatures (<500 °C). Arsenic is also largely volatilised (~51–79%) at low temperatures but to a lesser extent than Se. The remaining As is substantially volatilised upon increasing temperature to 1100 °C. The extent of As volatilisation is greater under gasification conditions than under pyrolysis and combustion conditions, particularly within the temperature interval 700–1000 °C. Zn, Pb and Sb are largely volatilised (>90%) with increasing temperature from 700 to 1100 °C. The gas atmosphere appears to have only a minor influence on the volatility of these elements. V, Mn, Cu, Co, Ni and Be all have low volatilities below 1100 °C. These elements become enriched in the ash (or char) residues during pyrolysis, combustion and gasification.

Batch leaching tests demonstrate that the trace elements Se, As, Zn, Sb, Mn, Cu and V are partially water extractable in the ash dam water algae. With the exception of V, the leachability of these elements is generally reduced following thermal conversion. Vanadium can be 4–5 times more leachable in combustion ashes than in the corresponding algal feedstock. Pb and Be are practically insoluble in both samples of algae and in their thermal conversion residues. The influence of combustion temperature on the leachability of the trace elements is complex. The different trace elements respond in different ways to increases in combustion temperature and the trends are not consistent between the two samples of algae. The influence of gas atmosphere is clearer. The trace elements are significantly less leachable in residues prepared under pyrolysis and gasification conditions than in residues prepared under combustion conditions at the same operating temperature (1000 °C).

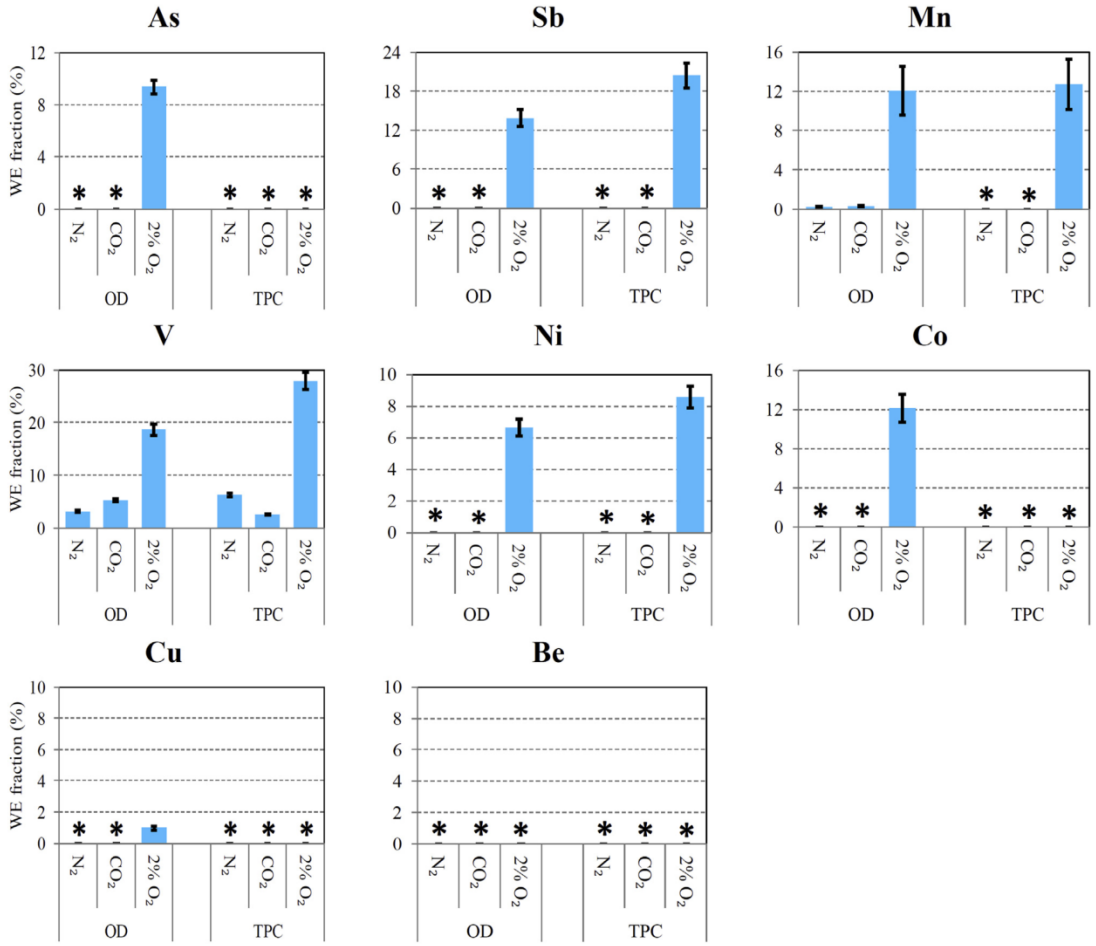

Fig. 9. Water extractable (WE) fractions of selected TEs in thermal conversion residues prepared at 1000 °C under pyrolysis (N_2), combustion (2% O_2/bal. N_2) and gasification (CO_2) gas atmospheres. Results are presented for OD and TPC. Error bars represent ± 2 standard deviations. Values marked with an asterisk (*) are below the limit for accurate detection.

Acknowledgements

This project was supported by the Australian Research Council's Linkage Projects funding scheme (project number LP100200616) with our industry partner SQC Pty. Ltd., the Australian Government through the Australian Renewable Energy Agency (Funding Agreement numbers Q00150 and 002369), the Advanced Manufacturing Cooperative Research Centre, funded through the Australian Government's Cooperative Research Centre Scheme and the MBD Energy MACRO Research Program.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.biombioe.2015.09.013.

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Supplementary data

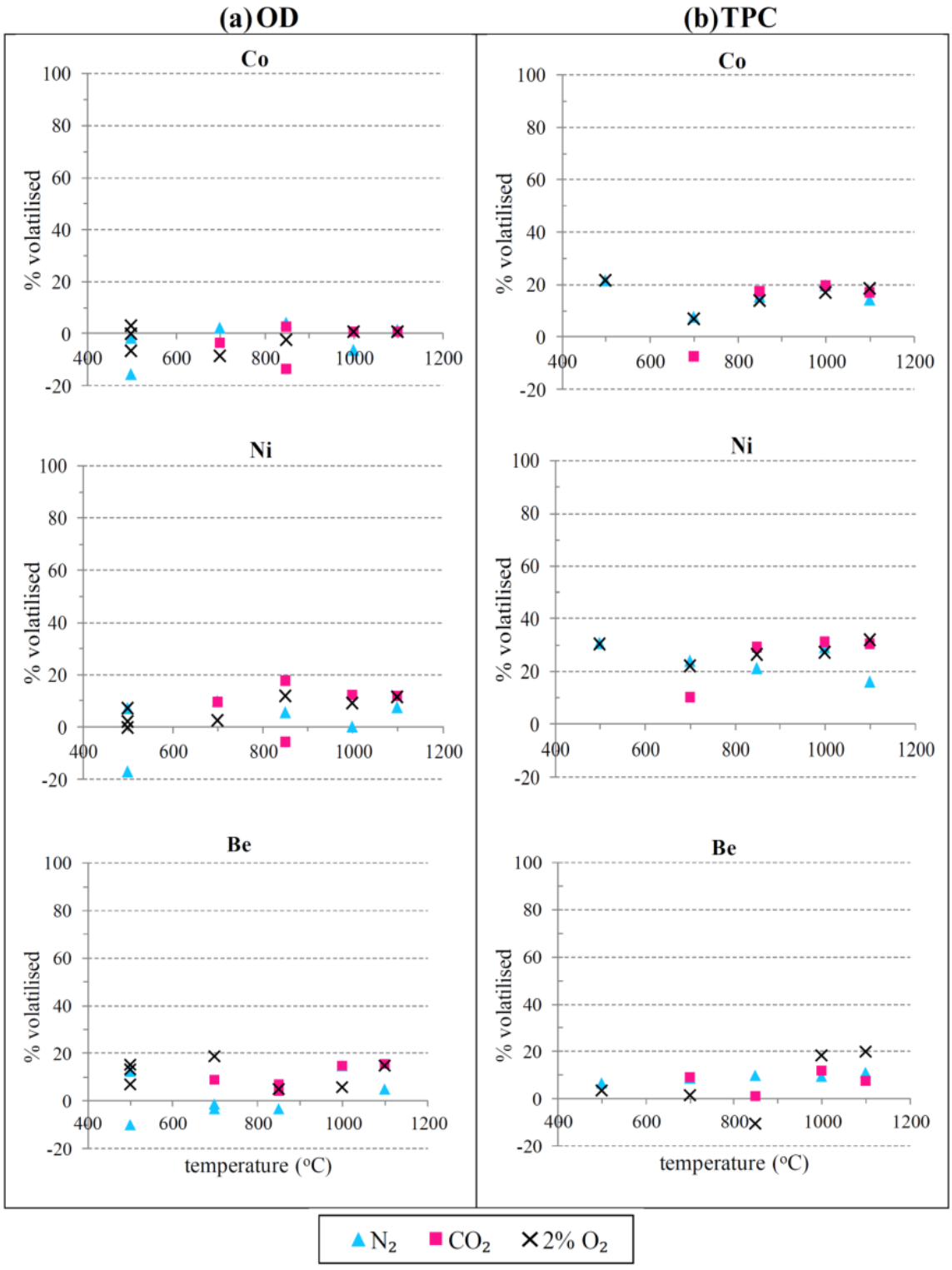

Figure A1. Volatilisation of Co (top), Ni (middle), and Be (bottom) from OD (a) and TPC (b) as a function of reactor temperature. Data are presented for pyrolysis (N_2), combustion (2% O_2/bal. N_2), and gasification (CO_2) gas atmospheres. Note that data is not shown for CO_2 at 500 °C.

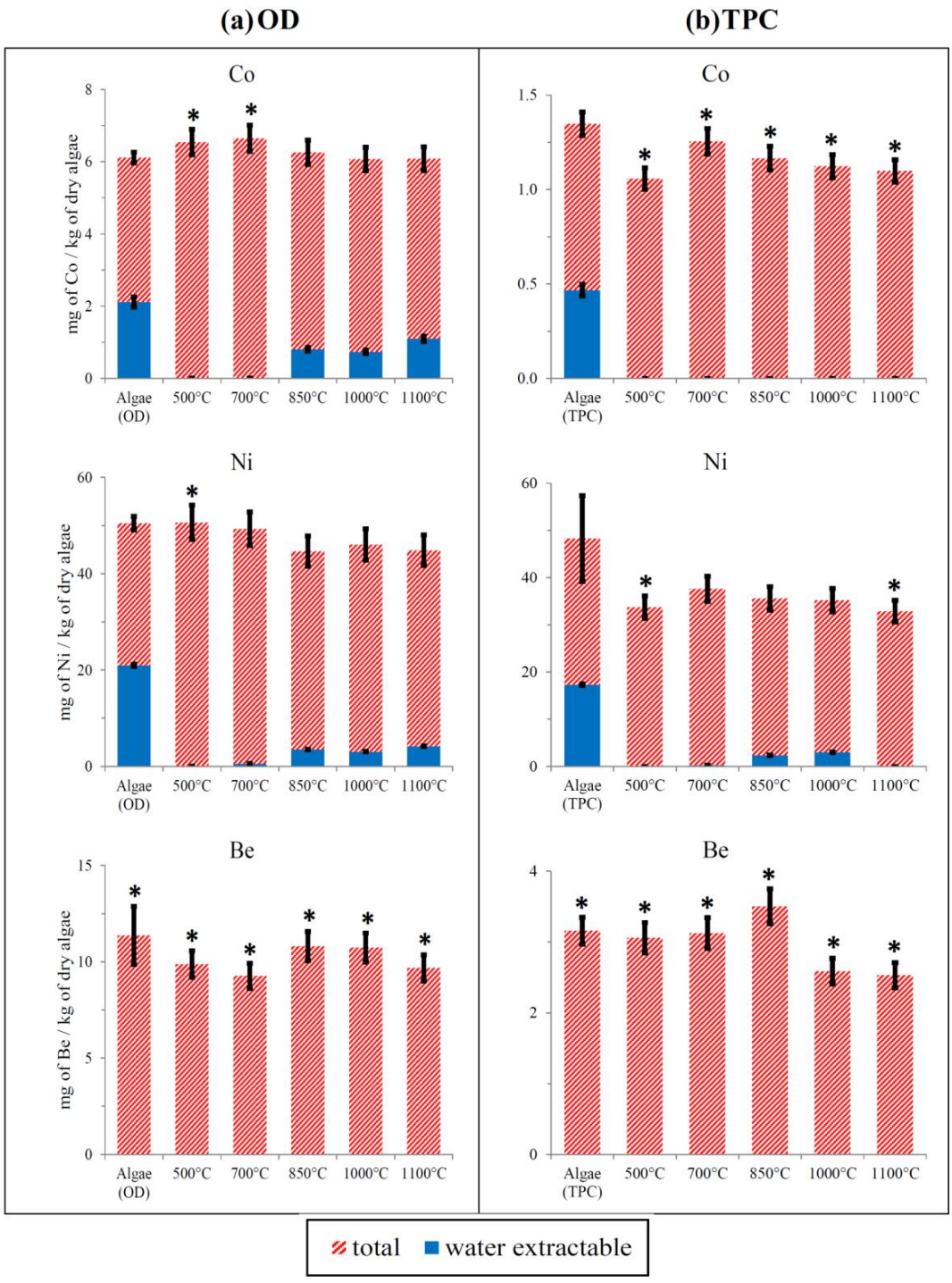

Figure A2. Leachability of Co (top), Ni (middle), and Be (bottom) in ADW algae and in combustion ashes prepared at various temperatures. Results are presented for OD (a) and TPC (b). All data are expressed as mg kg^{-1} of dry algae ± 2 S.E. An asterisk (*) is used to indicate where the water extractable concentration is below the limit for accurate detection (0.2 mg kg^{-1}). Differences in the y-axis scales for OD and TPC account for the different concentrations of the TEs in the two algae.

Chapter 7

Conclusions and Recommendations

7. Conclusions and recommendations

7.1. Conclusions

This thesis advances the knowledge of the thermochemical fuel behaviour of micro- and macroalgal biomass. The outcomes of this thesis can be broadly categorised into the following areas of fuel particle conversion:

- Oxidation of carbon and char reactivity
- Conversion of fuel-N
- Occurrence of the inorganic elements
- Bed agglomeration
- Release of volatile inorganic elements
- Mobilisation of trace elements

This section presents specific conclusions in each of these areas based on the results presented in this thesis.

7.1.1. Oxidation of carbon and char reactivity

The total conversion of C to CO and CO_2 exceeded 84% during the combustion of fixed-bed samples of micro- and macroalgal biomass. In most cases, a greater proportion of the total C was released during devolatilisation rather than during char oxidation. The gasification (CO_2) reactivity of algal chars varied for different species of algae and for different cultivation environments. The reactivity of the chars all increased with increasing extent of char conversion. This result has positive implications for achieving complete conversion of the chars in practical systems. The char reactivity measurements and the partitioning of released C between volatiles and char, collectively enable improved predictions of the extent of carbon burnout in industrial-scale thermochemical reactors.

7.1.2. Conversion of fuel-N

High levels of N were measured in one sample of microalgae (6.7% N, dry and ash-free basis) and in three samples of macroalgae (1.5 – 7.6% N, dry and ash-free basis). The total conversion of fuel-N to NO during fixed-bed combustion ranged between (6 – 21 g of N / 100 g of fuel-N), and was found to diminish with increasing content of fuel-N. In most cases, emissions of NO were predominately released during devolatilisation rather than during char oxidation. The results from this study provide a basis for the

development of strategies to mitigate emissions of NO during the combustion of algal biomass.

7.1.3. Occurrence of the inorganic elements

The relative proportions and occurrence modes of the main inorganic elements in algal biomass were largely dependent on the cultivation environment. The leaching behaviour of these elements indicated a high proportion of inorganic, water-soluble, alkali salts in all of the algae tested. Sodium was the main alkali metal in the marine algae and K the main alkali metal in the freshwater algae. By comparing the water-leachable fractions of cation forming elements to that of anion forming elements, it was inferred that the Na in marine algae occurs mainly as NaCl. This was supported by scanning electron microscopy and X-ray diffraction analyses on biomass and ash samples. The K in freshwater algae likely exists as a number of different salts. The alkali salts present in both marine and freshwater algae are expected to cause operational problems in industrial reactors such as fouling, ash deposition, corrosion, and bed agglomeration.

7.1.4. Bed agglomeration

Experimental simulations of algal ash interactions with quartz bed material indicated that melt-induced agglomeration, involving the binding of inert bed particles with an ash-derived melt, is the principal mechanism for bed agglomeration during fluidised-bed (FB) combustion of algal biomass. The composition and adhesive behaviour of the ash melt was found to vary for different species of algae and for different cultivation environments. The marine algae formed salt-based melts and the freshwater algae formed silicate-based melts. The presence of phosphate inclusions in the silicate melt appeared to increase the tendency for the ash to stick to the quartz particles. Based on the outcomes from this study, it is expected that bed agglomeration will be largely controlled by the formation of molten ash on bed particles during combustion, rather than ash chemically reacting with the bed particles.

7.1.5. Release of volatile inorganic elements

Differences in the release of S, Cl, K, and Na were significant between marine and freshwater species of algae but were only minor between micro- and macroalgal species. Sulphur was released in two steps. Part of the S was released at low temperatures (<500 °C). The balance was released at higher temperatures during

combustion and gasification, but was partially retained in the char residue during pyrolysis. The fraction of S released at low temperatures was greater for the freshwater algae (~70 – 85%) than for the marine alga (~30%). In the case of the marine alga, Cl and the alkali metals, K and Na, were more or less completely volatilised with increasing temperature from 700 to 1100 °C. These elements were released in almost identical proportions within this temperature interval, presumably by sublimation of alkali chlorides. In the case of the freshwater algae, the release of Cl was high (~55 – 65%) at low temperatures and was disproportionate to the release of the alkali metals. It has been proposed that Cl is dissociated from the alkali metals and then released as HCl vapour. The release of the alkali metals was relatively low. Only ~20 – 35% of the total K and ~35 – 50% of the total Na was released below 1100 °C. Volatilisation of melted alkali phosphates has been suggested. The behaviour of P was similar for both marine and freshwater algae. Phosphorous release commenced at around 850 °C under pyrolysis, combustion, and gasification conditions, and by 1100 °C, between 40 – 70% of the total P had been released. The release of Cl, S, P, K, and Na is intimately connected with fouling, ash deposition, and corrosion in industrial thermochemical reactors. The results from this study therefore provide vital knowledge for the prediction and mitigation of these problems.

7.1.6. Mobilisation of trace elements

The mobility of 11 trace elements (As, Be, Co, Cu, Mn, Ni, Pb, Sb, Se, V, Zn) during the thermal conversion of two samples of ash-dam cultivated algae has been assessed. Selenium was predominately volatilised (~79 – 97%) at low temperatures (<500 °C). Arsenic was also largely volatilised (~51 – 79%) at low temperatures but to a lesser extent than Se. The volatility of As was enhanced by operating in a reducing gas atmosphere, particularly within the temperature interval 700 – 1000 °C. Zn, Pb, and Sb were mainly volatilised between 700 and 1100 °C. Differences in gas atmosphere had only a minor influence on the volatility of these elements. The following elements all displayed low volatilities below 1100 °C, regardless of the gas atmosphere: Be, Co, Cu, Mn, Ni, and V.

All of the trace elements investigated, except for Be and Pb, were partially extracted from the algae during batch leaching. Vanadium was up to 4 – 5 times more leachable in the combustion ashes than in the corresponding algal feedstocks. The other trace elements were generally less leachable following thermal conversion. The trace

elements were more stable in residues prepared under pyrolysis and gasification conditions than in residues prepared under combustion conditions.

The results from this study show that emissions of most of the investigated trace elements can largely be prevented by limiting the operating temperature to 700 °C. However, this approach will have little impact on emissions of Se and As, since these elements substantially volatilise at low temperatures. Other control measures, such as the use of sorbents, will likely be needed to reduce emissions of Se and As to acceptable levels. The results from this study also show that several trace elements have potential to be released into the environment in significant quantities post thermal conversion, by means of leaching from char and ash residues. The quantities leached can be substantially reduced by operating in an inert or reducing gas atmosphere, rather than in an oxidising gas atmosphere.

7.2. Recommendations for future work

Contributions have been made within several areas of fuel particle conversion. However, additional studies are still needed in order to develop a comprehensive understanding of the thermochemical fuel behaviour of micro- and macroalgal biomass. Recommendations for these studies are outlined below:

- One inherent feature of algal biomass is high moisture content. It is well known that fuel moisture affects various aspects of fuel particle conversion such as char reactivity [162, 163] and the release of volatile inorganic elements [135, 136]. Relatively dry samples of algal biomass (no more than 12% moisture) were used in the experiments presented in this thesis. However, if algal biomass is to be used in commercial thermochemical processes, the biomass will likely contain higher levels of moisture, since the use of a wetter feedstock reduces costs associated with biomass drying. Therefore, future combustion and gasification experiments should utilise algal samples with higher moisture contents.

- Nitric oxide (NO) is generally the main oxide of nitrogen emitted during the combustion of biomass fuels [70]. However, in FB combustors, nitrous oxide (N_2O) can also be emitted in significant quantities [95]. N_2O contributes to the greenhouse effect and to the depletion of ozone in the stratosphere [94]. Therefore, it is recommended that N_2O be measured in addition to NO during

the combustion of algal biomass. Measurements of reduced species, particularly NH_3 and HCN, are also recommended. The measurement of these species under different operating conditions will shed light on the mechanisms governing the formation and destruction of NO and N_2O during combustion.

- Preliminary experiments, involving heating pellets consisting of algal ashes mixed with quartz particles, were used to simulate interactions that take place between algal ashes and bed particles during FB combustion. One limitation of these experiments is that the quartz particles were kept in constant contact with the ash. This poorly simulates conditions inside a FB reactor where both the ash and bed particles are in constant motion. Thus, the next step towards improving understanding of bed agglomeration processes during the FB combustion of algal biomass is to carry out combustion experiments in a laboratory-scale FB reactor from which bed material is periodically sampled. Such experiments would reveal the temporal development of agglomerate formation and provide deeper insights into the mechanisms governing bed agglomeration.

- The release of Cl, S, P, K, and Na to the gas phase was quantified by means of mass balances based on elemental analyses of laboratory-prepared char and ash residues. Direct measurements of these elements in the gas phase would help to reveal not only the timing of their release but also the species which they are released as. This additional knowledge would greatly help in developing a mechanistic understanding of the release of the inorganic elements, which is ultimately needed for the effective control of ash-related issues in industrial-scale thermochemical processes. A number of technologies could be used to measure the inorganic elements in the product gases such as molecular-beam mass-spectrometry [54] and advanced laser-based techniques [164].

- Only a select number of trace elements were addressed in the study on the mobilisation of trace elements during the thermal conversion of ash-dam cultivated algae. The behaviour of B, Cr, and Mo was not investigated. These elements occur in ash-dam cultivated algae in high concentrations and are all

potentially toxic when present in the environment at elevated levels [165]. Therefore, the mobility of these elements should be studied in future work.

- Certain species of algae are capable of sequestering high levels of various trace elements from industrial wastewaters (*e.g.* effluent from metal processing industries and ash-dam water). Many of these elements become highly concentrated in the ash (or char) residues following the thermal conversion of algal biomass. An extension to the work presented in this thesis could be to assess the technical and economic viability of recovering these elements from the ash (or char) residues.

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