



Thermochemical Fuel Behaviour of Micro- and Macroalgal Biomass

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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 CO₂ 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 CO₂ 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 (N₂, 2% O₂, and CO₂) 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.

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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.