A Systems Approach to Thermochemical Conversion and Carbon Sequestration from Microalgae

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Declaration

I certify that the work in this thesis entitled “A Systems Approach to Thermochemical Conversion and Carbon Sequestration from Microalgae” has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree to any other university or institution other than Macquarie University.

I also certify that the thesis is an original piece of research and it has been written by me. Any help and assistance that I have received in my research work and the preparation of the thesis itself have been appropriately acknowledged.

In addition, I certify that all information sources and literature used are indicated in the thesis.

Signed: 

Scott Richard Grierson (Student Id# 41108884)

Date: 28th November, 2012

“On the arid lands there will spring up industrial colonies without smoke and without smokestacks; forests of glass tubes will extend over the plains and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but that will have been mastered by human industry which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurry, and mankind is.”

- Giacomo Ciamician, *Science*, 1912 -

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To my family and friends I owe eternal gratitude for their unwavering support, encouragement and belief over an extended period of life's trials and tribulations.

Dedication

This work is dedicated to all those committed to a sustainable future, in whose trust and courage I continually draw my inspiration.

"You are capable of more than you know. Choose a goal that seems right for you and strive to be the best, however hard the path. Aim high. Behave honourably. Prepare to be alone at times and to endure failure. Persist! The world needs all you can give."

- E. O. Wilson -

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Abstract

Energy supply and demand, coupled with mounting evidence regarding anthropogenic climate change and the need to find sustainable alternatives to consumption of fossil oil, place biomass resources in a position of unique prominence given the fundamental carbon capture mechanism inherent in plant photosynthesis. In navigating a transition to a sustainable energy future, biomass also offers the prospect of leveraging existing infrastructure, knowledge and investments while potentially reducing the greenhouse gas intensity of many of our activities, through refining of transport biofuels and renewable electricity production. However, the availability of terrestrial biomass resources other than agricultural or forestry wastes and weedy species for these applications is highly contentious, especially where human population is booming and food production is likely to assume increasing amounts of productive land.

Microalgae are an aquatic biomass alternative that can be cultivated in a range of water sources and climatic conditions, promising high productivity per unit area, without the need to occupy productive land. Furthermore, the pyrolysis processing of microalgae presents an opportunity to combine a highly productive source of biomass with the means to produce renewable bio-oil and biogas, in addition to biochar, that can be used to sequester carbon in soil. Taken together, this offers the potential to deploy a solution that may be able to net reduce atmospheric carbon dioxide levels, while producing considerable economic and societal value and avoiding food commodity conflicts.

Six species of microalgae (*Tetraselmis chui*, *Chlorella like*, *Chlorella vulgaris*, *Chaetocerous muelleri*, *Dunaliella tertiolecta* and *Synechoccocus*) were initially selected for study, representing a broad cross-section of physical characteristics and known behaviour under cultivation. The objective of this preliminary investigation was to ascertain differences in thermal conversion behaviour between these microalgae species under slow pyrolysis conditions.

The samples were first analysed with a Computer Aided Thermal Analysis (CATA) technique at a standard heating rate of 10°C/min. For all species, the energy required to achieve thermal conversion was found to be approximately 1MJ/kg. Gas chromatography was then applied to measure the evolution of biogas compounds with temperature. The heat of combustion of the biogas compounds was estimated to vary significantly between species, ranging from 1.2 to 4.8 MJ/kg. Pyrolysis oil product yields were also estimated at 500^{o}C. The oils produced at this temperature were collected and their molecular weight distribution assessed by Matrix Assisted Laser Desorption/Ionisation (MALDI). The species were found to produce up to 43% by volume of bio-oils. In all samples the char fraction remained above one third of total sample weight.

The oil and char derived from the slow pyrolysis of the unicellular marine green alga *Tetraselmis chui* were then further analysed in detail, using a variety of techniques. The pyrolytic oil fraction exhibited a wide variety of fatty acids, alkanes, alkenes, amides, aldehydes, terpenes, pyrrolidinines, phytol and phenols, with a high heating value (HHV) of 28 MJ/kg. The biochar produced has a HHV of 14.5MJ/kg and reveals a number of properties that are potentially valuable from an agronomic point of view, including high cation exchange capacity (CEC), large concentration of N, and a low C:N ratio. The quantity of C in *T. chui* biochar that can be expected to stabilise in soil amounts to approximately 9%/wt of the original feedstock, leading to a potential net reduction in atmospheric CO_2.

Examining ways to innovate the microalgae cultivation and processing value chain includes a focus on the most efficient and economical means to extract the liquid oil fraction from the microalgae species. Additional work compares the use of organic solvent, supercritical carbon dioxide (SC-CO_2) and pyrolysis to assess their relative capacity to derive oil from the marine microalgae, *Tetraselmis chui* (*T. chui*). SC-CO_2 technique was shown to be least effective in natural oil extraction from *T. chui* due to the polarity of compounds but nevertheless demonstrates the feasibility of this concept. The results revealed that pure solvent extraction produces the most complete

extraction of natural oil at just under 15% by weight. Subsequent pyrolysis of post-solvent extraction residue and examination of by-products suggest that extraction of natural lipids prior to thermal processing increases the total quantity of bio-oil yield production by more than 11%.

Life cycle assessment (LCA) of a microalgae biomass cultivation, bio-oil extraction and pyrolysis processing regime is a useful means to gauge the likely environmental impact of this prospective new development on an industrial scale. Coupled to thermal conversion via slow pyrolysis, the prospect of biologically ‘sequestering’ carbon derived from microalgae biomass as biochar, added to soil, is considered. However, an intensive closed culturing photobioreactor system coupled to a pyrolysis process incurs a net increase in global warming impact and life cycle impact, notwithstanding biochar application to soil. Results indicate that up to 50% of environmental impact in certain categories stems from the upstream influence of fertiliser production. Energy used in flue gas delivery and pumping during cultivation is also considerable, suggesting that current practice in closed cultivation systems does not yet adequately trade-off biomass productivity against operating intensity. Drying of the harvested microalgae biomass for pyrolysis processing is potentially a major hurdle in terms of process viability also. Overall, utilisation of nutrients derived from waste streams, integrating renewable energy and capture of process heat for more efficient drying are essential levers for reducing the environmental impact of this proposition before it can be declared of net benefit to society.

List of Publications

The following is a list of publications derived from this thesis with declaration of authorship contributions outlined in Appendix A.

Journal Articles

Grierson, S., Strezov, V., Ellem, G., McGregor, R. & Herbertson, J. 2009. Thermal characterisation of microalgae under slow pyrolysis conditions. *Journal of Analytical and Applied Pyrolysis,* 85, 118-123.

Grierson, S., Strezov, V., & Shah, P. 2011. Properties of oil and char derived from slow pyrolysis of Tetraselmis chui. *Bioresource Technology,* 102, 8232-8240.

Grierson, S., Strezov, V., Bray, S., Mummacari, R., Danh, L.T., & Foster, N. 2011. Assessment of Bio-oil Extraction from Tetraselmis chui Microalgae Comparing Supercritical CO2, Solvent Extraction, and Thermal Processing, *Energy &* Fuels, 26 (1), pp 248-255.

Grierson, S., Strezov, V., & Bengtsson, J. 2013. Life cycle assessment of a microalgae biomass cultivation, bio-oil extraction and pyrolysis processing regime, *Algal Research*, 2 (3), pp 299-311.

Peer-reviewed Conference Papers

Grierson, S., Ellem, G. & Strezov, V. 2007. “Microalgae as an Aquatic Biomass Alternative for Sustainable Energy and Materials Production”, peer-reviewed conference paper presented at the *Environmental Research Event*, Cairns, Australia.

Grierson, S. and Strezov, V. 2012. “Life Cycle Assessment of the Microalgae Biofuel Value Chain: A critical review of existing studies”, peer-reviewed conference paper presented at *The Third International Conference on Bioenvironment, Biodiversity and Renewable Energies*: *Bionature 2012*, St. Maarten, Netherlands Antilles.

Conference Presentations

Grierson, S. 2007. “Biomass Production in the Context of Climate Change: The Role of Algae in Sustainable Biomass Supply”, Session 4, *Bioenergy Australia Conference 2012: Sustainable Energy in a Carbon Constrained World*, Surfers Paradise, Australia.

Grierson, S. & Strezov, V. 2008. “Thermal decomposition, characteristics and behaviour of microalgae during slow pyrolysis”, Session 9: Analytical Pyrolysis Applications II, *Pyrolysis 2008: 18th International Symposium on Analytical and Applied Pyrolysis*, Lanzarote, Spain.

Conference Posters

Grierson, S. 2011. “Life Cycle Assessment of Microalgae Lipid Extraction Techniques”, poster presented at the *1st International Conference on Algae Biomass, Biofuel & Bioproducts*, St. Louis, United States of America

Chapter 1: Introduction

Biomass offers many attractive opportunities for fossil resource displacement, including alternative derivation of liquid transport biofuels and carbon abatement. Unlocking a low impact, high volume biomass solution for energy and materials production is an important consideration as part of an integrated, strategic response to the challenges of sustainable development. Aquatic microalgae represent a highly productive source of biomass that could avoid many of the issues associated with terrestrial biomass cultivation and harvest by utilising non-productive land, waste nutrients, carbon dioxide, and non-potable water. They are highly adapted to a variety of environments and can be grown in fresh, saline, brackish or even wastewater streams, across a variety of temperature ranges.

Pyrolysis of microalgae presents an opportunity to combine a highly productive source of biomass with the means to produce renewable bio-oil and biogas, in addition to biochar, that can be used to sequester carbon in soil. Taken together, this offers the potential to deploy a solution that may be able to net reduce atmospheric carbon dioxide levels, while producing considerable economic and societal value. However, before launching a scaled microalgae and pyrolysis processing industry, it is necessary to first consider the broader environmental impacts that this system might represent.

In this work, life cycle assessment (LCA) techniques are used to translate fundamental scientific data relating to thermochemical processing behaviour of a candidate microalga, *Tetraselmis chui*, along with a scaled model for production, into a baseline understanding of the likely environmental impact of this proposition. The study has a specific focus on a photoautotrophic cultivation system coupled to intensive ‘point source’ carbon emissions, combined with slow pyrolysis processing, with the intention of investigating in detail the potential for high volume biological carbon capture and sequestration (bio-CCS) through production of biochar in an industrial ecology setting.

Use of LCA-oriented benchmarking is increasingly common in the fast moving consumer goods (FMCG) manufacturing industry and is useful for driving continuous improvements in environmental performance towards sustainable outcomes. Ultimately, using LCA techniques to guide decision-making and systematic innovation of an end-to-end microalgae cultivation and processing value chain will help to ensure that this proposed regime is able to deliver a net benefit to society and the environment, at any scale of adoption.

Essentially, the critical question at the heart of this investigation is whether or not microalgae biomass, when combined with pyrolysis processing, can be sufficiently scaled to a level that could have a material impact on fossil resource consumption and indeed atmospheric carbon dioxide levels, without lurching industry from one fundamentally unsustainable paradigm to another. The contingent factors of embodied impact of all process inputs across the system are important to consider in totality and relate to the fundamental premise that the microalgae biomass proposition must be able to be carbon neutral or better, in order to obtain a social license to operate and be justified on both environmental and commercial grounds. Notably, a focus on carbon masks a number of additional environmental impacts that can also have a profoundly negative influence at industrial scale, hence it is important to broaden the scope of analysis to ensure these are also considered.

There is no prospect that a ‘microalgae-to-slow pyrolysis’ regime would alone form a sufficient solution to anthropogenic, macro-environmental problems such as climate change, acidification or eutrophication. There are many sustainable innovations that will be required, introduced systematically over an extended period, to address the nature and scale of these challenges. Nevertheless, to refer to the ‘wedges’ theory (Pacala & Socolow, 2004), and to the extent that marine microalgae in particular are already a global force of nature in terms of their impact on the carbon cycle, there is the possibility that this could be developed into a technical response of considerable scale. The overriding argument here is linked to the ‘value-adding’ potential of efficient biomass utilisation, including the ability to produce fossil energy offsets and with slow pyrolysis in particular, the biological carbon capture and storage

(bio-CCS) capacity of biochar production and application. This vision represents a compelling means to address the carbon abatement challenge in a way that can simultaneously unlock economic, social and environmental value – a truly sustainable outcome.

Chapter 2 aims to review the literature that underpins this thesis, spanning the relevant socio-political, strategic and most of all, scientific context in which this work has unfolded. This includes briefly coming to terms with contemporary environmental and sustainability discourse, reviewing the rationale for biomass as a strategic platform for working towards a sustainable future, introducing microalgae as an important candidate for biomass feedstock, providing background on the pyrolysis process and considering prior analytical work undertaken in relation to pyrolysis of algae, before finally defining the body of life cycle assessment (LCA) studies to which this work aims to make a contribution. This chapter is largely comprised of two published peer-reviewed conference proceedings, Grierson, S., Ellem, G. & Strezov, V. 2007. “Microalgae as an Aquatic Biomass Alternative for Sustainable Energy and Materials Production”, a peer-reviewed conference paper presented at the *Environmental Research Event*, Cairns, Australia and, Grierson, S. and Strezov, V. 2012. “Life Cycle Assessment of the Microalgae Biofuel Value Chain: A critical review of existing studies”, a peer-reviewed conference paper presented at *The Third International Conference on Bioenvironment, Biodiversity and Renewable Energies*: *Bionature 2012*, St. Maarten, Netherlands Antilles.

Chapter 3 chronicles early experimental and analytical work that explores the thermochemical decomposition behaviour of a range of microalgae biomass samples (both marine and freshwater) with a particular focus on biogas, bio-oil and biochar decomposition ratios under slow pyrolysis conditions. This chapter also considers the process energy balance of achieving decomposition within the target temperature range using a novel thermal analysis technique and thereby derives the (stoichiometric) energy yield of the evolved volatile gases with a view to offsetting these input requirements. In its entirety, this chapter represents the journal paper, Grierson, S., Strezov, V.,

Ellem, G., McGregor, R. & Herbertson, J. 2009. “Thermal characterisation of microalgae under slow pyrolysis conditions”, *Journal of Analytical and Applied Pyrolysis,* 85, 118-123.

Chapter 4 represents an extensive experimental campaign undertaken to characterise both the bio-oil and biochar fractions derived from slow pyrolysis of *T. chui*. The work provides greater insight into the specific make up of each of these by-products and in particular presents a range of analytical data relating to the agronomic properties and abatement potential of the biochar fraction. This work has been published as Grierson, S., Strezov, V., & Shah, P. 2011. “Properties of oil and char derived from slow pyrolysis of Tetraselmis chui”, *Bioresource Technology,* 102, 8232-8240.

Chapter 5 considers a non-invasive oil extraction technique using supercritical carbon dioxide that focuses on the natural lipids produced by *T. chui*. The purpose of this approach is to explore whether maximum liquid yield can be derived from the biomass resource by carefully removing the high purity lipids prior to pyrolysis processing (that might otherwise be effectively gasified at low temperature), to then produce bio-oil and biochar from the residue (assuming that the biogas is directed toward energy recovery). The alternative is to pyrolyse the raw, dry harvested microalgae biomass directly and this work weighs up the two options to determine the optimum processing regime, based on analytical data. The chapter is a reflection of the published paper, Grierson, S., Strezov, V., Bray, S., Mummacari, R., Danh, L.T., & Foster, N. 2011, “Assessment of Bio-oil Extraction from Tetraselmis chui Microalgae Comparing Supercritical CO2, Solvent Extraction, and Thermal Processing”, *Energy &* Fuels, 26 (1), pp 248-255.

Chapter 6 synthesises all of the analytical data with known sub-unit processes for the cultivation, harvesting and processing of microalgae into a detailed life cycle inventory, from which a life cycle model can be built. This lays out a number of different processing routes and applies an adapted life cycle impact assessment (LCIA) methodology to gauge the aggregated environmental impact of each pathway and to compare the direct extraction and pyrolysis

process outputs with incumbent and alternative products. This work was submitted and subsequently underwent major revisions following peer review, prior to resubmission, as Grierson, S., Strezov, V., & Bengtsson, J. 2013, “Life cycle assessment of a microalgae biomass cultivation, bio-oil extraction and pyrolysis processing regime”, *Algal Research,* 2 (3), pp 299-311.

Finally, Chapter 7 offers concluding remarks and recommendations that reflect on the outcomes of the study.

In the main, this thesis is a compilation of a series of interlinked, published studies and conference papers that have been systematically subjected to peer review. As such, the format of each of the chapters is retained and largely preserves the integrity of the respective journals in which they have been published. The overall intent is to present a comprehensive analysis of the thermo-chemical decomposition behaviour and properties of *Tetraselmis chui* microalgae and its pyrolysis by-products, based on analytical methods, that follows a logical progression of thought in order to arrive at a final conclusion regarding the implications for industrialisation.

Chapter 2: Literature Review

2.1 Energy Supply and Demand

The International Energy Agency (IEA) projects that the global demand for primary energy is expected to increase from an annual of 2650 million tonnes oil equivalent (Mtoe) by approximately a third over the period to 2035, with the majority of this demand growth coming from developing nations (2011d). In contrast to this demand projection, the Association for the Study of Peak Oil (ASPO) has for some time highlighted that there is a fundamental disconnect between the amount of investment in oil exploration and refining, and known reserves and deposits, the majority of which are in production decline (Skrebowski, 2004). Globally, we are faced with a looming energy constraint, especially in relation to liquid transport fuels, that will only escalate unless a reliable supply of replacements for fossil oil can be found.

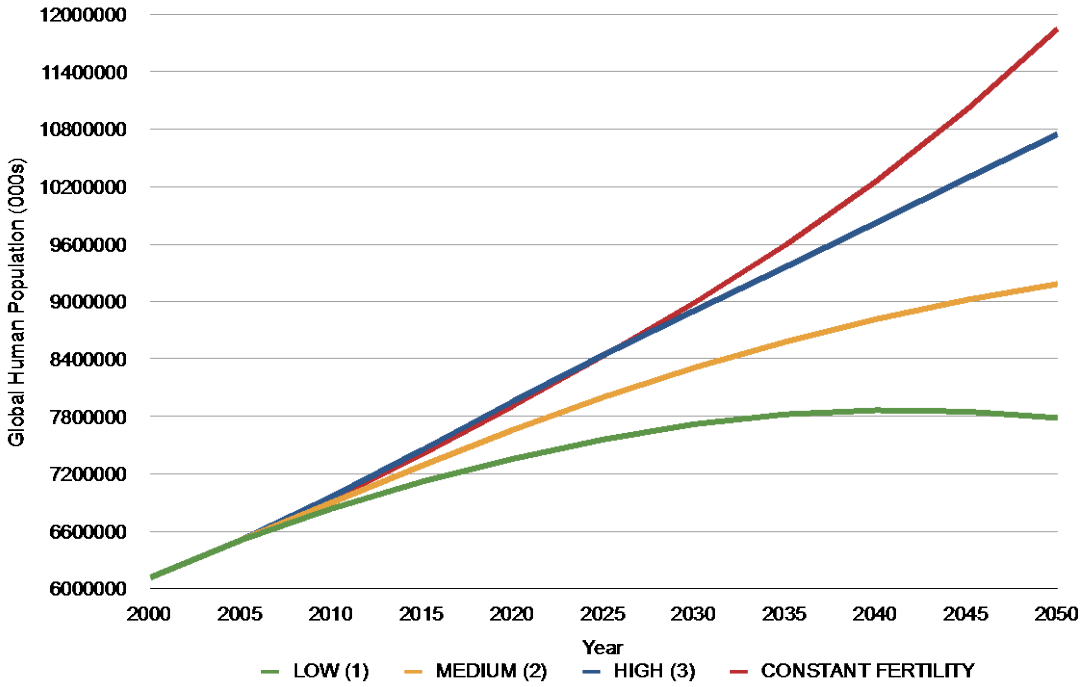


Figure 1. UN Population Revision 2006 (Thousands)

A further dynamic in the mix relates to human population (Figure 1), which is projected to increase to somewhere between 7.8 and 10.7 billion globally by 2050, based on recent estimates (2007c). Population trends and GDP growth

have shown a strong correlation, leading to a systematic increase in consumption of products and resources (Table 1). In turn, the relationship between GDP growth and CO_2 emissions suggests that the traditional economic advantage afforded by fossil fuels has been fundamental to building wealth and prosperity since the advent of the industrial age (Tucker, 1995). Although the measurement and basis of this relationship is contentious, the historical evidence suggests therefore that it is difficult to 'decouple' economic growth from carbon emissions intensity (de Bruyn et al., 1998; Rothman, 1998).

Table 1. Global Population and Consumption Trends, 1950-2000 [derived from (Bhalla, 2002; Meadows et al., 2005)]

Metric	**1950**	**2000**	**1950~2000**
Human Population (billions)	2.52	6.07	247%
Global Gross Domestic Product (GDP) (Billion USD/day, purchasing power parity)	17	107.5	632%
Registered Motor Vehicles (millions)	70	723	1,030%
Oil consumption (million barrels/yr)	3,800	27,635	727%
Natural gas consumption (trillion cu. ft./yr)	6.5	94.5	1,454%
Coal consumption (million metric tonnes/yr)	1,400	5,100	364%
Electricity generation capacity (GW)	154	3,240	2,104%
Corn (maize) production (million metric tones/yr)	131	594	453%
Wood Pulp production (million metric tone/yr)	12	171	1,425%
Iron Production (million metric tones/yr)	134	580	433%

2.2 Anthropogenic climate change and the carbon abatement challenge

Greenhouse gas emissions and climate change potentially place an additional constraint on energy consumption that is in many ways more pressing than supply (Raupach et al., 2007; Truffer & Fahnestock, 2007). Rapid increases in the concentration of atmospheric greenhouse gases emanating from human combustion of extracted fossil resources are now widely acknowledged as a key driver of climate change (Persic, 2006; Bates et al., 2006; Solomon et al., 2007). These anthropogenic emissions are systematically increasing in concentration in the atmosphere and serve to amplify the natural 'greenhouse effect' (Bates et al., 2006; Raupach et al., 2007). The net result is a rise in global mean temperature that may severely disrupt weather cycles and lead to unpredictable or even catastrophic climate events (Solomon et al., 2007; Truffer & Fahnestock, 2007). In short, "the world is facing twin energy-related threats: that of not having adequate and secure supplies of energy at affordable prices, and that of environmental harm caused by consuming too much of it" (2006).

Climate change represents an unprecedented risk to modern civilisation and the arguments for urgent remedial action are compelling. There have been many high-profile proposals and theories put forward in recent years that seek to acknowledge and address carbon emissions in macro-economic, political and conceptual terms (Socolow et al., 2004; Stern, 2006). Technical responses are also necessary to reduce carbon emissions with a view to long term transition to a sustainable energy platform, including adoption of 'next generation' fossil technologies (Kharecha & Hansen, 2007).

The Economics of Climate Change, otherwise known as 'The Stern Review' (Stern, 2006), was based on the assumption that even if a 30% reduction in global CO_2 emissions could realistically be achieved by 2020, atmospheric stabilisation of CO_2 at 450 ppm by 2050 equates to 135 billion tonnes of $CO_{2\text{-}e}$ ($GtCO_2$ equivalent) in abatement products, services and infrastructure being brought online over the subsequent decade to 2030. Once this 'interim' target

is achieved, there is at least an additional 1,400 billion tonnes of carbon abatement that must also be achieved between 2021 and 2050 to reach the long-term stabilisation goal. In order to meet this, innovation and rapid escalation of sustainable alternatives to existing sources of fossil energy must occur on an unprecedented scale (Hoffert et al., 1998).

2.3 Strategy and Sustainability

Under the prevailing global economic and political paradigm, there appears to be a conflict between numerous competing consumer and population trends, with known socio-ecological threats and the need to address them (Hannesson, 2002; Asif & Muneer, 2007). The current focus on climate change in contemporary discourse suggests that it is somehow a direct *cause* of social, economic and ecological instability. An alternative viewpoint is that from a systems perspective, rapid observed changes in the earth's climate are rather *symptoms* of a fundamentally unsustainable societal paradigm that systematically violates the minimum requirements for successful, healthy function of (human society within) the biosphere (Holmberg, 1999; Robèrt, 2000; Robèrt et al., 2002). Therefore, if an atmospheric stabilisation target of 450ppm $CO_{2\text{-}e}$ or similar is believed to be the maximum threshold beyond which dangerous and potentially irreversible earth system changes will take place, then humanity has an overriding strategic constraint within which to plan for the future.

By adopting a systems approach grounded in 'backcasting', it is possible to envisage a wide array of sustainable futures based on shared principles for socio-ecological success (Holmberg, 1999). 'Backcasting' from an envisioned future to the present, based on 1st order principles that form strategic planning constraints (representing minimum requirements for successful and healthy functioning of socio-ecological systems) enables strategic planning towards a sustainable vision to take place in a way that maintains a relationship between all levels of a system (Broman et al., 2000). That is, decisions or actions taken at either a micro (e.g. home, small business) or macro (e.g. government

policy, corporation) level have equal relevance and integrity if kept consistent with these same 1st order principles.

Such a planning orientation is highly relevant to managing the transition away from dependence on fossil resources to support sustainable development of industry and society. Adoption of a backcasting orientation in our energy system ensures that systematic progress towards sustainability can be made, whilst continuing to innovate and create value throughout the transition period across a broad portfolio of possible options (Robinson, 1982). Biomass in particular offers a unique opportunity for establishing a 'flexible platform' that is able to utilise legacy hydrocarbon infrastructure and can help to bridge the gap to a sustainable future, simultaneously leveraging knowledge, technology and expertise that can reduce the embodied environmental impact of incumbent fossil energy and materials dependency, at acceptable cost and in timely fashion.

2.4 Biomass resources

Examination of the scale and nature of the global carbon abatement challenge suggests that unlocking a sustainable, high volume alternative for energy and materials production is an important consideration as part of an integrated, strategic response. Many of the technical breakthroughs in the increasingly mainstream and economically competitive solar, wind and geothermal technologies are encouraging. Yet these technologies are designed to address stationary electricity generation only and out of all renewable energy options, only biomass can also viably substitute the material feedstock demand for the valuable products traditionally derived from fossil resources, such as liquid fuels, plastics, fabrics, fertilisers and chemicals (Chaumont, 1993). As such this places biomass in a unique and critical position of relevance to global society.

Biomass technologies offer a compelling way to harness cyclic, biospheric carbon. Carbon is captured and stored in plant cells through photosynthesis or found in organic waste steams (both plant and animal) in a diverse array of

biomolecules such as lipids, carbohydrates, proteins or nucleic acids (Ragauskas et al., 2006). For each gram mole of carbon fixed through photosynthetic activity, it is calculated that around 470 kJ (112 kcal) of energy is captured (Klass, 2004). These molecules can be extracted, broken down and/or processed to obtain 'energy carriers' in the form of liquid fuels for use in combustion engines, including ethanol or biodiesel, or to provide a substitute for petro-chemical material feedstocks for use in industry (Sims et al., 2006; Sanders et al., 2007; Demirbas et al., 2009). Biomass can also be combusted directly in specialised industrial plants to provide both heat and electricity, providing another means of offsetting fossil energy consumption.

From a liquid transport fuels perspective, biomass can directly address diffuse 'tailpipe' emissions due to upstream absorption of CO_2 during photosynthesis. Advantages of developing renewable biomass substitutes for fossil fuels are that they have a similarly high energy density and are easy to store and transport. They can also blend with existing liquid fuel systems and avoid the requirement to reconstruct a vast and capital-intensive infrastructure for distribution, retailing, engineering and end-use.

A balanced analysis of existing societal assets and a range of possible climate change responses suggests that biomass is a highly advantageous option in a move towards sustainability (Fernandez-Reiriz et al., 1989; Klass, 2004). The transition to a sustainable biomass platform has the promise of being relatively seamless for the general public in terms of infrastructure and products, as long as production and cost can be controlled through technological innovation and appropriate market incentives. It represents a significant strategic step forward from the present by leveraging an existing societal energy and materials platform into a new realm of sustainable innovation.

2.5 Biomass and biofuel production in Australia

Many countries around the world do not have the possibility of becoming self-sufficient in liquid transport biofuel supply as they are fundamentally

constrained by available land (for biomass production) relative to population density and demand. Australia has neither of these factors as a constraint, yet despite being a net energy exporter (coal and gas), as a nation Australia is now heavily reliant on the import of liquid hydrocarbons for transport fuel as domestic fossil oil production has declined with diminishing reserves (Love & Cuevas-Cubria, 2007).

The growth potential for biofuel production in Australia was examined in a publication released by the CSIRO on behalf of the Rural Industries Research and Development Corporation (O'Connell et al., 2007). This report cites greenhouse gas emissions, fuel security, land and water benefits, public health and benefits to regional areas as key drivers of change towards a biofuel industry. Successful realisation at the upper limit of CSIRO projections could substitute for up to 1468.4 PJ of energy, delivered as ethanol and biodiesel. This equates approximately to all current domestic liquid fuel consumption and represents around 20% of Australia's current total energy use.

However, the 'best case' projected biofuel production figures in the CSIRO report are heavily reliant on ligno-cellulosic ethanol processing, which is currently an immature technology and not yet commercially operational. The figures also indicate a skew in the fuel mix away from diesel engines that underpin the mining, agricultural and heavy transport industries in Australia.

It is also worthy of note that the combined production capacity (as opposed to actual production output) of biofuels in Australia in 2005 reported by the Prime Ministerial 'Biofuels Taskforce' was estimated at 90.7 ML (O'Connell et al., 2005). The projections in this report were that with aggressive growth and expansion, this could have reached 1,529 ML by 2010 (1005ML ethanol and 524ML biodiesel). Due to a prolonged drought and the rising cost of feedstock the actual output of biofuels in 2005/06 was only 41ML ethanol and 16ML biodiesel (Love & Cuevas-Cubria, 2007).

Realistically, the outlook for biofuel production in Australia is likely to be restricted to the production of fuel blends unless an additional source of high volume biomass and viable processing technologies can be developed. A blended transport fuel market (B20, E10) would certainly improve Australia's current overall carbon emissions profile, however, not to the extent that necessary reductions towards a global CO_2 stabilisation target of 450ppm would be achieved. Even with the most optimistic assumptions about improvements in efficiency, yield, investment, technology, environmental conditions (soil, rainfall, adverse weather) and logistics, it is difficult to believe that the potential for biofuel production in Australia will not continue to be subjected to factors that reduce overall output below production capacity. As it stands therefore, the limitation for Australian biomass is more related to sustainable growth and availability of biomass than production capacity or the size of the domestic transport fuels market.

2.6 Environmental challenges and production constraints of biomass utilisation

The extent to which biomass will be able to provide an alternative energy and materials platform remains unclear. Studies suggest that the total amount of biomass on the planet is considerable and far exceeds our current annual energy consumption (Klass, 2004). However, much of this biomass is unavailable for reasons of high conservation value, critical function as carbon sinks, soil integrity, accessibility or competition with existing food crops (Moreira, 2006).

Net primary productivity (NPP) is a measure of the amount of biomass produced by photosynthetic plants on earth, less that effectively consumed by the plants themselves during respiration. The greatest concentration of earth's NPP is centred on the equator and is most pronounced in the rainforests of the Amazon basin of Brazil, also currently the world's major producer of sugar cane-derived bioethanol (Figure 2). Equatorial rainforest in Africa, Borneo, the Malay Peninsula and the Indonesian archipelago is likewise of global biomass significance, where much of the world's growing palm oil industry is now

based. Bioenergy crops such as palm oil and sugar cane, increasingly geared to the production of liquid transport fuels, assume large tracts of land, consume significant resources and can produce a substantial greenhouse debt during establishment (Ulgiati, 2001).

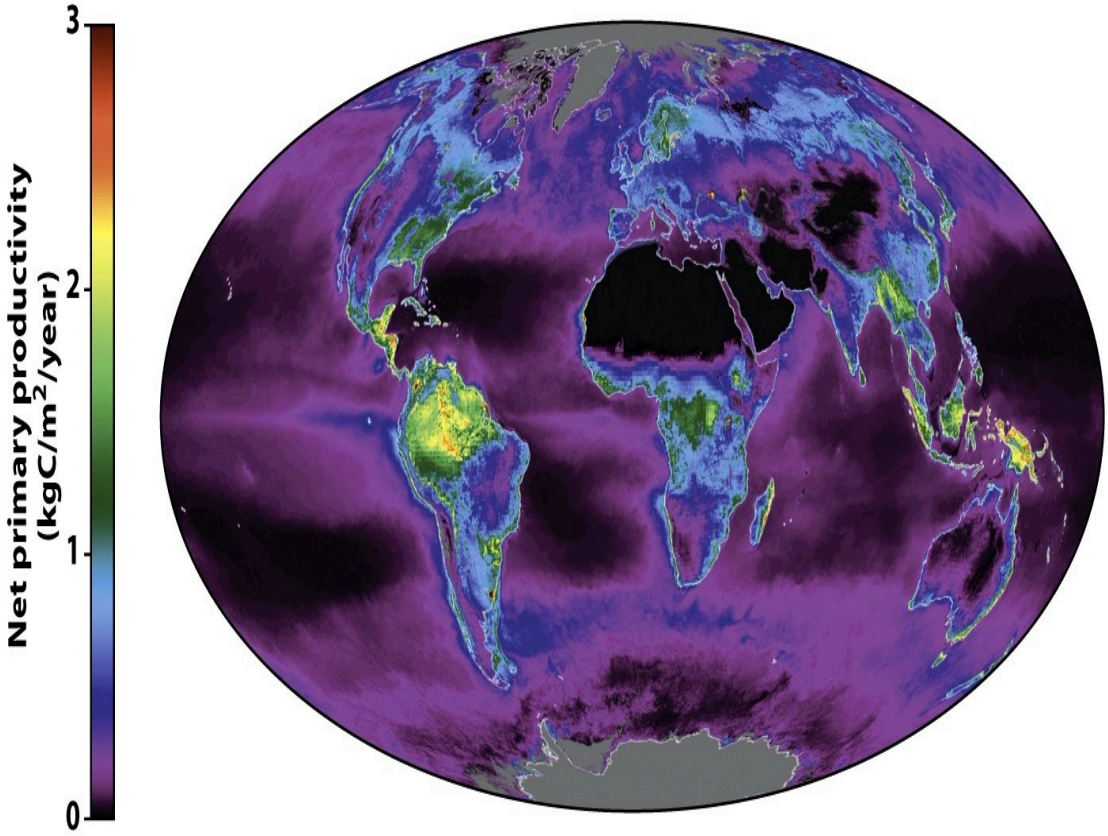


Figure 2. Global Net Primary Productivity (Freeman & Hamilton, 2005)

The mounting competition between energy and food production could also bring about radical changes in land use such that regions of high NPP and biodiversity will become increasingly valued for biofuel production (Laurance, 2007; Peskett et al., 2007). Widespread land clearing of equatorial rainforest in response to biofuel demand continues to occur, eroding the world's largest remaining terrestrial CO_2 sinks and threatening unique ecosystems (Porteous & Mogg, 2006).

The issue of nutrient availability further complicates sustainable biomass output. The more reliant society becomes on biomass resources, the more we

need to improve management of critical plant growth nutrients, including nitrogen and in particular, phosphorous (Cordell et al., 2009). For arid countries like Australia, freshwater availability for supporting crop production is also a critical constraint, further jeopardising the viability of the biomass industry.

As the greenhouse gas advantages of biomass and its energy and material by-products are increasingly valued, it is possible that supply and delivery of biomass for processing will come under pressure as demand increases (Rathmann et al., 2010). Land availability and yield levels in energy crop production have been identified as primary limiting factors for industrial biomass production (Berndes et al., 2003). Detailed analysis of the broader implications of biomass production interacting with all dependent variables is necessary in order to make any realistic assessment about commercial viability. This has implications for strategic planning and is necessary to understand the complex web of connected issues such as land management, food production, economic impact, existing biomass use, water consumption, soil condition, biodiversity, habitat conservation, nutrient and carbon cycles that must all be taken into account.

2.7 Food versus Fuel

A major disadvantage for cultivation of bioenergy crops is competition with food supply. Current technology for biofuel production provides a ready pathway for extraction or refinement of the inherent sugar or lipid content of many food crops into bioenergy products, such as liquid transport fuel. One US study found that dedicating all current US production of corn and soy to biofuel production would only meet 12% and 6% of domestic gasoline and diesel demand, respectively (Hill et al., 2006). Regardless, price volatility of food and energy markets are intrinsically linked where they share a common resource. In recent years, demand speculation in biofuel markets has led to rapid spikes in commodity prices such as maize (corn) in the Americas, which has had far reaching socio-economic implications, not least for developing countries within the region (Runge & Senauer, 2007).

These competing demands also have ‘knock on’ effects throughout the agricultural sector. As oilseeds and grains are diverted to biofuel production, upward price pressure affects their use as livestock feed also, adding to the baseline cost of producing other agricultural commodities (Mues et al., 2007). Furthermore, meeting basic human needs through the provision of adequate nutrition poses a difficult challenge that must be prioritised. Any growth in demand for biomass is therefore currently facing the challenging prospect of significant limitations in relation to industrial production on the one hand, and, worse still, the creation of a new, fundamentally unsustainable paradigm on the other.

A study by Hoodwijk et. al. (2003) reviewed the contribution that biomass could potentially make to future energy supplies, with a view to 2050. Calculations were based on the amount of agricultural land devoted to food production globally, representing direct food/feed production or related pasture. This figure was estimated at 5Gha globally, with other categories of land use and terrestrial biomass production such as forestry or other bioenergy production considered separately. In any case, only land classed by Hoodwijk et. al. as ‘Category 1’ was taken into account for the viable production of biomass, with biofuels notionally relegated to cultivation only on surplus agricultural land.

In considering the availability of productive agricultural land for the cultivation of ‘1st generation’ biofuel crops, further consideration is given here to the sizeable differences in the intensity of the overall food production system in relation to servicing a vegetarian, moderate (limited meat) and affluent diet, high in meat and dairy products (Penning de Vries et al., 1995). The increased intensity associated with meat and dairy products relates directly to the higher trophic level from which these products derive, representing a concentration of embedded energy and consumption of resources up the food chain. These figures are expressed in MJ day^{-1} of energy intake and are converted into grain equivalent in kg dry weight/day for comparison (Table 2). Notably, this dietary analysis also reflects the tendency for GDP (‘affluence’)

to be reflected in the eating habits of humans, who demonstrably increase their protein intake (mostly through consumption of meat & dairy products) with increasing wealth (with the exception of cultural or religious edicts that may prevent this).

Table 2. Global average daily consumption per adult for three different diets expressed in MJ/day and as grain equivalents in kg of dry weight/day (based on Penning de Vries et. al., 1995)

	Veg Diet	**Moderate Diet**	**Affluent Diet**
Energy intake (MJ $^{d-1}$)	10.1	10.1	11.5
Plant production (gr. Eq. kg^{-1} d^{-1})	1.05	0.90	1.13
Meat production (gr. Eq. kg^{-1} d^{-1})	-	0.22	1.91
Dairy production (gr. Eq. kg^{-1} d^{-1})	0.28	1.23	1.16
Total (gr. Eq. kg^{-1} d^{-1})	**1.3**	**2.4**	**4.2**

A further important variable relating to agricultural productivity is the difference between what are termed 'Low External Input' (LEI – minimal use of chemicals, irrigation, artificial fertilisers and pesticides) and 'High External Input' (HEI – applying 'best technical means' wher e nutrient supply is mostly from fertilisers, intensive weed, pest and disease control applied, and irrigation is widespread) scenarios. These scenarios suggest an average annual agricultural output per hectare of 3.1 tonnes of grain equivalent in the LEI scenario, which is in similar order to the world average productivity figure in 2000, based on FAO data (2002). This contrasts with the 5.9 tonnes ha^{-1} yr^{-1} assumed for the HEI scenario, providing an estimated maximum global production output of grain equivalent in Gton for both the LEI (12Gt/yr) and HEI (35.6Gt/yr) scenarios.

By introducing low (1), medium (2) & high (3) UN population forecasts (2007c), we are then able to convert world food demand to 2050 for the 3

dietary scenarios into an energy equivalent, and to compare this with actual food production capacity (LEI & HEI regimes) over the same period, which takes into account the calculated human requirement for food intake of an equivalent 9.4 MJ/day (Table 2).

The approach adopted by Hoodwijk et. al. (2003) is to allow a 'food security factor of 2' to account for losses in transport, storage, variation in production output from year to year, unequal income distribution that affects capacity to purchase, and other factors – here also adopted. Hence, this approach conservatively doubles the food demand equation to allow for variations in the food system and to provide a necessary buffer.

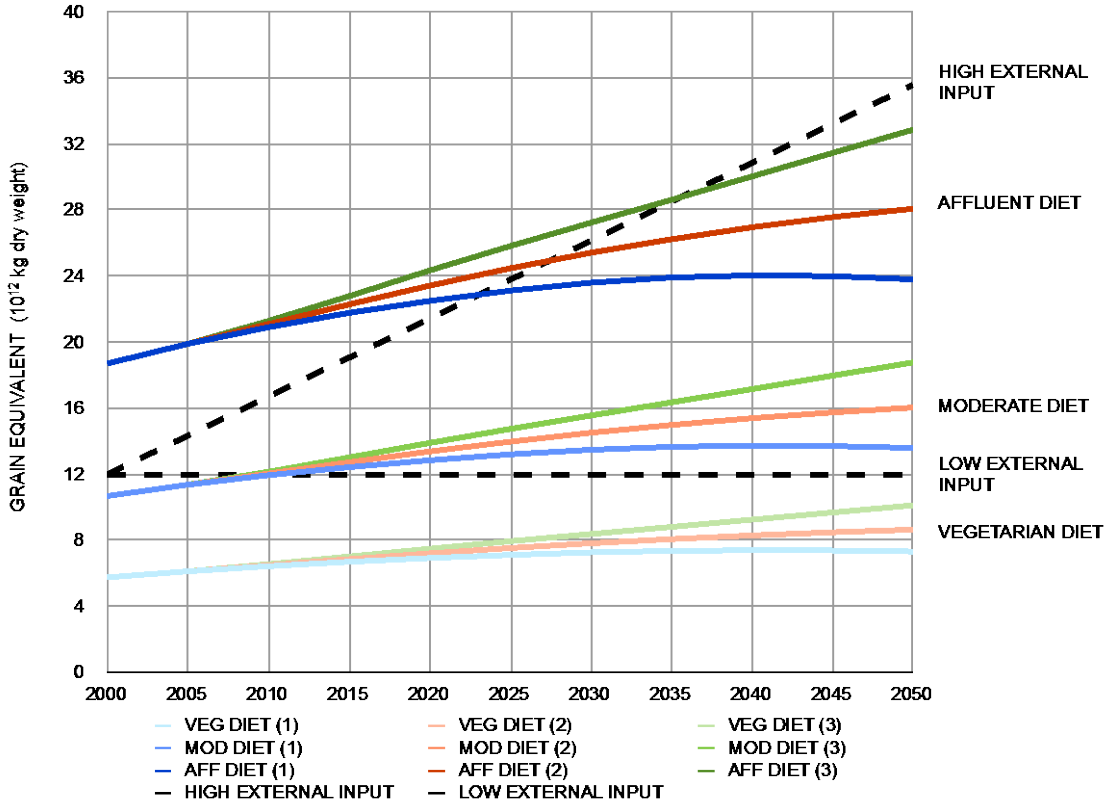


Figure 3. World food demand vs. supply with food security factor of 2 (based on diet & intensity of the production system)

The result of this synthesis is presented in the graph above (Figure 3). The known production capacity of the global food system in 2008 (12.6Gt grain equivalent p^{-1} y^{-1}) is already close to being exceeded by the food demands of an increasing global population (which in turn, is close to a moderate diet

equivalent of consumption). However, based on average dietary intake and food security factors, this does not imply that the world's entire population has now uniformly adopted a moderate protein diet. Since much of the world's population (including China and India) is still relatively poor and known to subsist on a predominantly vegetarian diet, this means that conversely the developed world, representing a much smaller albeit more affluent fraction of the global population, accounts for the bulk of the meat and dairy protein consumption reflected in the average.

From Figure 3, we can see that a vegetarian diet and a LEI food production system could support a growing global population to 2050 and beyond. Any significant proportion of meat present in the global diet however requires an increase beyond the LEI production threshold. Only significant ongoing improvements in food production capacity can hope to meet growing demands, due to increasing wealth (change in dietary profile) and increasing human population (mouths to feed). The multiplying life-cycle effect of a HEI scenario in terms of fresh water, energy, emissions and nutrients is likely to be significant, also placing additional pressure on an expansion of agricultural land beyond the base of 5Gha. In any case, the prospect of this level of production being achieved globally is highly optimistic and represents a 'best case' scenario.

A key insight relevant to the interpretation of the primary data presented (Figure 3) relates to the HEI scenario. As a maximum *theoretical* production output, we can only assume that this will require significant ongoing improvements in food technology and farming practice from the present level until 2050, at which point peak productivity would be reached. In reality, the production threshold in the HEI scenario presented in Figure 3 is likely to be somewhat more dynamic, however is represented here as a linear 1.4% annual increase in productivity from 2000 to 2050. It should be noted that this equates to an approximate worldwide doubling of food output per unit area of land during this period, requiring a significant leap in food production as per the 'green revolution' of the 1960's and 1970's.

The future food supply projections raise concerns about the prospect of large-scale shifts in dietary habits that may accompany rising GDP in the developing world and the explosive nature of the increased food production demand that would commensurately be placed on natural resources. Obviously, such a development will place additional burden on the food production system, over and above an increase in population. What this equates to in global terms is a colossal multiplier effect in food, energy and water consumption that places additional demand on productive agricultural land, as well as process nutrients.

Questions must also be asked about the vulnerability of the global food system to climate change and how this might continue to impact food security and output. Recent evidence suggests that agricultural systems and food production are under increasing pressure from climate change, with as much as 30% of the world's population considered 'food insecure' (Brown & Funk, 2008; Lobell et al., 2008). Evidence also suggests that this leads to inequality in the distribution of localised environmental impacts associated with food production (White, 2000), most keenly felt in the developing world due to its dependence on small-scale subsistence agribusiness and the influence of global commodity markets. While climate change impacts on food output observed since the early 1980's are small relative to the technical yield gains achieved over the same period, this illustrates that negative impacts are already occurring and have been for some time, on a global scale.

Importantly, the capacity of '1st generation' food crops to contribute to the production of liquid fuel substitutes (assuming we are all fed) highlights the need to seek alternative sources of biomass supply. Figure 4 presents the projected energy demand in oil equivalent (IEA, 2007) with the land devoted to food crops under a medium (2) population scenario, and in relation to all three dietary profiles. Human civilisation is already achieving LEI-equivalent productivity yet consuming at a moderate diet-equivalent. Therefore, assuming no substantial increase in net agricultural productivity in the near future, we can expect to soon have a food shortfall, let alone have excess food crops or land available for bioenergy production. In the 'best case' HEI

scenario, assuming that global average diets don't change, it would be possible to produce only a maximum of 80 EJ in liquid biofuels (with no losses in conversion or processing) in 2050, less than a quarter of projected demand.

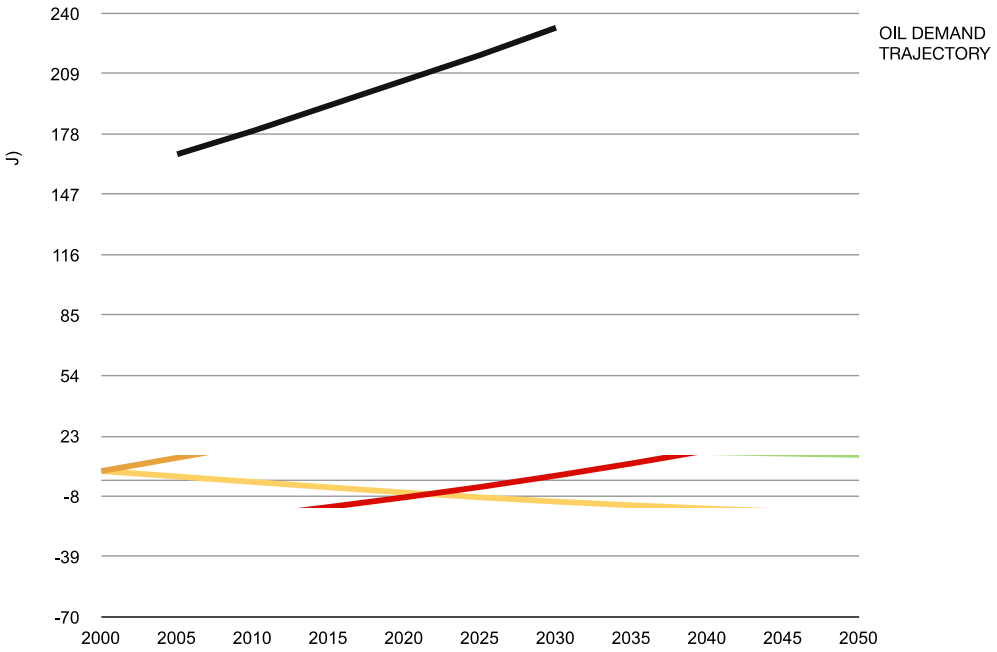


Figure 4. Global available bioenergy from excess food crops vs. oil demand equivalent (medium [2] population forecast; LEI vs HEI productivity)

Whatever the shortcomings of this crude illustration, or indeed the assumptions on which it is based, the message is that a focus on food crops for the production of bioenergy is only likely to escalate conflicts within commodity markets and adversely affect food output. It will also continue to put pressure on clearing of equatorial rainforest and other regions of high net primary productivity (NPP). The implication in terms of sustainable development is that it is counter-productive to rely on existing food crops (or land increasingly valued for their production) to meet biomass feedstock requirements. If we are to feed a growing human population, maintain the integrity of our remaining terrestrial carbon sinks and preserve the remaining biodiverse regions of our planet, we are increasingly dependent on marginal land for production of non-food competing bioenergy crops. If biomass is to

take a significant role in the future of our energy and material feedstock requirements, as well as contribute to the mega-tonnages required for meaningful carbon abatement, this also implies a growing reliance on the evolution of '2nd generation' biomass production and processing methods such as ligno-cellulosic conversion if we are to meet the looming shortfall in fossil oil.

A central question to be addressed ties together the issues of energy demand, peak oil, population growth, GDP and food production, in the context of climate change and carbon abatement. That is, as fossil oil supply begins to be exceeded by demand, what potential will there be for '1st generation' food crops to fill this gap and yet still meet the basic subsistence needs of a growing human population? What sustainable biomass alternatives are there and what will be the life cycle impact of their industrial cultivation and use, in terms of potentially escalating demand for primary resources and increasing carbon emissions, directly or indirectly?

2.8 Microalgae: an aquatic biomass alternative

2.8.1 Fundamental biology and characteristics of microalgae

Aquatic microalgae are regarded as one of the earliest forms of life on Earth and marine phytoplankton in particular are at least as important to the global carbon cycle as terrestrial plants (Wu et al., 1999b). Two species of microalgae alone are estimated to be responsible for as much as two-thirds of all CO_2 fixation in the oceans, equating to approximately one-third of global net primary productivity (Bryant, 2003).

The term "microalgae" refers to a broad classification of single-celled, microscopic prokaryotic (blue-green algae) and eukaryotic plants, of which the most prominent are the green (*Chlorophyta*), red (*Rhodophyta*) and diatom (*Bacillariophyta*) algae (Walker et al., 2005; Brennan & Owende, 2010). They are highly adapted to almost all environments and grow in fresh, saline, hypersaline, brackish or even wastewater streams, across a variety of temperature ranges and climate extremes. Microalgae represent a diverse

variety of distinct species, albeit display a basic cell structure that has enabled them to adapt and survive in almost every habitat imaginable. Species can be of either photoautotrophic (fix carbon through photosynthesis), heterotrophic (using other forms of organic carbon, such as sugars) or mixotrophic (capable of both photoautotrophic and heterotrophic) metabolic function (Brennan & Owende, 2010).

Commercial interest in microalgae stems from evidence that they are intrinsically more productive in terms of gross biomass yield per hectare when compared with terrestrial counterparts (Klass, 2004; Chisti, 2007; Gouveia & Oliveira, 2009) and can be refined into valuable products (Table 3). The inherent photosynthetic efficiency of autotrophic algal cultures means that they can capture CO_2 and generate biomass up to five times faster than plants grown in soil (Chen & Jiang, 2001). Furthermore, based on their functional requirements and nutritional profile, the approximate ratio of carbon, hydrogen and oxygen in algal biomass is such that for every 1kg produced, 1.83kg of CO_2 is taken up through photosynthesis (Grobbelaar, 2004).

Table 3. Examples of Biomass Productivity in t/Ha (Klass, 2004)

Switchgrass	***Maize (Corn)***	***Sugar Cane***	***Tropical Forest***	***Algae***
8-20	34.1	86.8	59.0	164.0

Their inherent CO_2 uptake efficiency make microalgae an especially promising biological candidate to address concentrated, point-source greenhouse gas emitters such as stationary power generators and heavy industry that produce vast quantities of CO_2 (Kishimoto et al., 1994; Benemann, 1997; Stepan et al., 2002; Wang et al., 2008). In addition, critical growth nutrients such as nitrogen and phosphorous can theoretically be obtained directly through wastewater and effluent streams, as well as via conventional fertilisers, presenting a suitable opportunity for industrial ecology

applications provided the necessary partnerships, agreements and scaled infrastructure can be realised (Pittman et al., 2011; Park et al., 2011).

In summary, aquatic microalgae represent a highly productive source of biomass that can sidestep many of the issues associated with terrestrial biomass production by avoiding use of agriculturally productive land and consumption of potable water. Taken together, this helps to address many of the identified shortcomings of terrestrial biomass production, potentially providing greater economic certainty and 'economies of scale' for industrial cultivation, with substantially reduced risks associated with climate change, food commodity conflicts and competition for fertile land (Carlsson et al., 2007).

2.8.2 Commercial products derived from microalgae

Despite the fact that microalgae have been exploited as a nutritional resource for thousands of years, relatively few species have been cultivated at an industrial scale to this point (Olaizola, 2003). Interest in mass culturing of algae reignited following the Second World War, when burgeoning population raised questions regarding the need to provide for growing human nutritional requirements and to address pollution issues (Tamiya, 1957). More recently, the debate has shifted to consideration of the potential for microalgae to be a source of high volume biomass that can be refined into bioenergy products, especially biofuels (Brown & Zeiler, 1993; Chisti, 2007; Beer et al., 2008; Li et al., 2008; Demirbas & Fatih Demirbas, 2011).

A number of promising algal species for biofuel production have been isolated, although the number of unexplored species far outweighs those that have been rigorously evaluated (Olaizola, 2003; Huang et al., 2010). Today, it is recognised that there are many possible applications for microalgae as a feedstock resource, from carbon abatement to production of specialty chemicals, cosmetics, nutriceuticals, animal feed, bioenergy and biofuels (Spolaore et al., 2006; Apt & Behrens, 1999).

Several studies of a broad selection of microalgae species have demonstrated that the biochemical composition of a microalgae culture differs according to the specific stage of its growth cycle and can even be manipulated to enhance the production of specific compounds (Fernandez-Reiriz et al., 1989; Brown, 1991; Zhukova & Aizdaicher, 1995). Genetic engineering of microalgae seeks to enhance oil yields per unit area by identifying key triggers of lipid production in target species (Douglas et al., 2003). Ultimately, successful exploitation of microalgae as a biomass resource requires a fundamental understanding of their behaviour under controlled cultivation conditions, in order to induce characteristics suitable for manufacture of desired end-product/s (Williams & Laurens, 2010).

To date, there have been few attempts to commercialise high volume production of algae strains for energy and material purposes as the growth variables are difficult to control at competitive cost (Molina Grima et al., 2003). The implication is that significant technical and economic innovation is required to unlock the microalgae biomass opportunity. Attempts have been made to culture high-yielding microalgae strains under controlled laboratory conditions, with a view to industrial production. These efforts rose to prominence with the 'Aquatic Species Program' run by the US Department of Energy between 1978-1996 (Sheehan et al., 1998). However replication of laboratory results in field applications has been notoriously difficult and presents numerous techno-economic challenges (Borowitzka, 1992; Walker et al., 2005).

2.8.3 Photoautotrophic cultivation systems

The opportunity for coupling to concentrated point source CO_2 emissions to achieve high volume carbon abatement, in addition to the desire to avoid the requirement to supply an additional carbon supplement (e.g. sugar) to the cultivation cycle, sets photoautotrophic systems apart from their more productive heterotrophic counterparts (Figure 5). 'Open culture' autotrophic farming of microalgae (e.g. in 'raceway' ponds) is generally low in technical sophistication and complexity, and is undertaken with no physical barrier between the culture and the environment, leading to greater variability in

biomass yield and the risk of contamination from wild species and bacteria (Moheimani & Borowitzka, 2006). However, such systems are well understood and can be established at a relatively low to moderate capital and operating cost (Borowitzka, 1999). In open systems, light is typically the limiting factor for growth as achieving adequate light-dark cycling and periodic exposure of all cells to optimum light is restricted to a horizontal plane, that is, the surface area of the growth medium (Brennan & Owende, 2010).

Figure 5. Indoor photoautotrophic cultivation of microalgae

'Closed culture' systems, or 'photobioreactors' (PBRs), wherein the culture is held within an enclosed space, either tubes, bags or vertical columns (Figure 6), enable increased control of growth variables, can reduce contamination and may deliver a higher yield of biomass per unit area, but traditionally come at a much greater capital and operating cost (Stewart & Hessami, 2005; Brennan & Owende, 2010). These systems can allow for greater light penetration to the culture, which aids photosynthesis (Tredici & Zittelli, 1998). Ultimately, the ability to maintain continuous algal culture and control key process variables such as temperature, pH, nutrient concentration, salinity, light saturation, reproduction rate and turbidity is complex and differs

depending on the design of cultivation system (Apt & Behrens, 1999; Mata et al., 2010).

Figure 6. Floating photobioreactor

2.8.4 Harvesting microalgae

Harvesting, incorporating pre-concentration, dewatering and drying stages, is another challenge in working with microalgae biomass as the individual plant cells are microscopic and grow in very large volumes of aqueous suspension from which they need to be separated to varying degrees, depending on the desired end-product (Wang et al., 2008). Electro-flocculation is one technique that can be utilised to achieve agglomeration of cells of select species to aid harvest (Tenney et al., 1969; Poelman et al., 1997). Utilisation and adaptation of techniques from the wastewater treatment and food processing industries provide further options. Addition of flocculants, either chemical or biological in origin, is one means to achieve pre-concentration in order to aid a separation process (Fogarty, 1981; Xu et al., 2011b). Conventional dissolved air floatation (DAF) systems are also of interest and are well known for their

capacity to remove suspended solids, including algae, from an aqueous stream (Knappe, 2004). Food and beverage style clarifiers and industrial centrifuges are also of potential use in this endeavour given their proven capacity, technical maturity and reliability, although the process energy requirements are typically high (Shelef et al., 1984).

Once concentrated and dewatered to a paste (between 10-30% solids content), various drying technologies can be employed to obtain a powdered microalgae product of low moisture content. Solar drying is one possibility that could be leveraged based on experience in developing countries in the agricultural sector, and could radically alter the process economics for microalgae (Kadam, 2002). Spray and freeze drying techniques are proven and can be very effective however these are very energy intensive (Kajiyama & Park, 2011). A comparison between a 'dry' and 'wet' processing route as the means to treat microalgae with a view to producing a liquid fuel product suggests that there are advantages and disadvantages in each, however the energy consumption involved in achieving a dry product is considerable and a major hurdle to overcome (Xu et al., 2011a). In the end, the final choice of harvesting options depends on a number of factors, including the morphology of the cells, density of the harvested culture and finally, the desired end product and therefore the 'budget' available for dewatering techniques based on process economics and overall intensity.

2.8.5 Processing pathways

Once harvested, algae biomass can be feasibly processed into useful fuels and other petro-chemical substitutes, however, no optimal pathway for this transformation has yet been identified (McKendry, 2002b). Utilisation of the harvested, dry biomass as a 'whole food' or animal feed product is possible without the need for additional processing and represents a considerable market in its own right, however this neglects the bioenergy and fossil oil displacement premise on which the prospect of scaled microalgae cultivation has traditionally been viewed. It is likely that multiple product and income streams will be necessary to support the growth of the microalgae industry in the short term, however capturing the high volume biofuel market remains a

long-term fossil resource displacement goal (Luque, 2010). Before this can be achieved, considerable innovation in cultivation, harvesting and processing technologies is required to make scaled production of algal biomass a reality and thereby to bring it to a level of competitive price parity with incumbent fossil resources (Gouveia & Oliveira, 2009).

For the purposes of this review and on the assumption that bioenergy products are the ultimate desired outcome from utilisation of microalgae biomass, there are a number of technical processing pathways that are of interest. Bioenergy in this sense encompasses both liquid fuels as well as electricity produced through utilisation of the biomass product. Opportunities for processing algae biomass present themselves as follows:

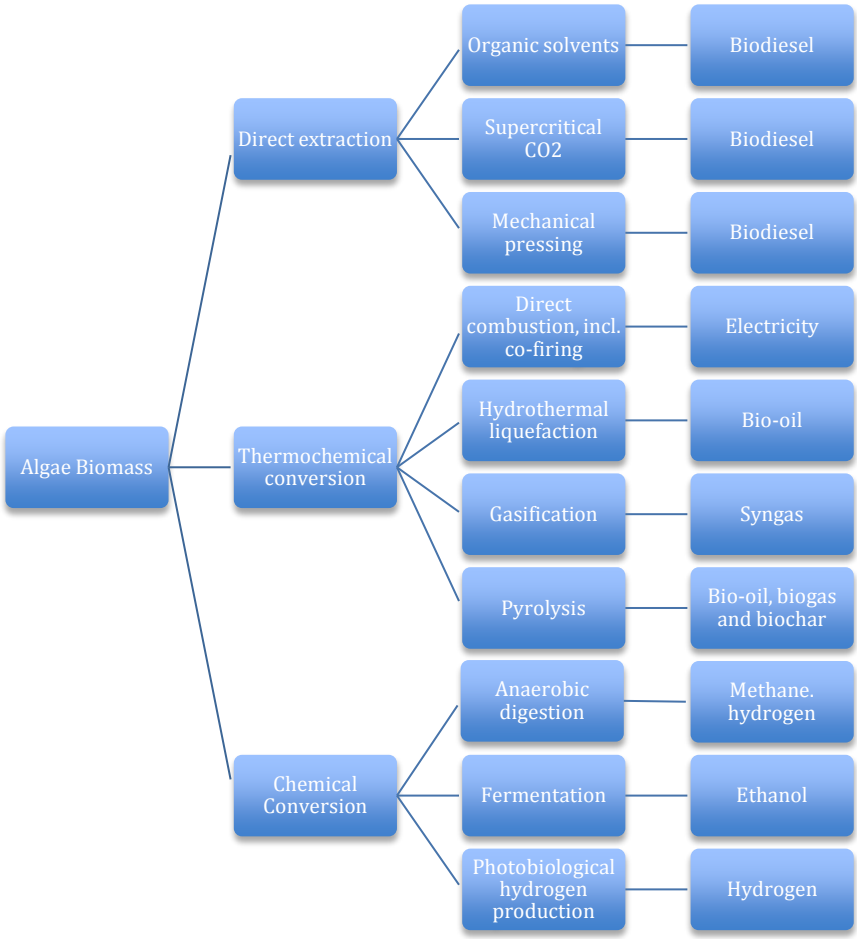


Figure 7. Algae biomass utilisation for bioenergy products, based on Brennan & Owende, 2010

Each of the options presented in Figure 7 above has distinct technical and operating requirements, with a wide variety of treatments also required for the upgrade or refinement of intermediary products, where applicable. A direct lipid extraction scenario for transesterification into biodiesel is fundamentally limited in terms of overall liquid yields because a microalgae culture high in lipids is by definition redirecting captured photosynthetic energy away from protein assembly and growth into storage, hence the productivity of the species is likely to suffer (Shifrin & Chisholm, 1981). While the extractable natural oil produced can be of high quality and purity, the overall capture of CO_2 in this regime is reduced accordingly, along with total liquid yields.

Therefore, microalgae species that favour biomass productivity and concomitant high carbon abatement potential may be of greater interest than those that are high in lipid content. Combined with a thermochemical conversion process, this approach need not compromise liquid yields overall especially given that the culture can be utilised in its entirety. Pyrolysis processing is one of several prospective thermochemical conversion techniques that has already been commercialised for the processing of biomass and waste materials that may have potential for use with microalgae.

2.9 Pyrolysis

Pyrolysis is a processing technique of heating material (in this case biomass) in the absence of oxygen to avoid combustion and thereby achieve thermochemical decomposition (Demirbas & Arin, 2002; Mulligan et al., 2009). The process is well established in the waste treatment industry and has a long history for the production of charcoal in agriculture dating back several thousands of years, where charcoal was made in primitive kilns or pits with a view to application to soil to improve its fertility (Sombroek et al., 2003; Lehmann et al., 2006; Balat, 2008).

Regardless of the heating rate, the generic process by which decomposition takes place can be defined by a series of discrete stages that occur with temperature increase (Grønli & Melaaen, 2000):

- An initial heat application to the biomass raises its internal temperature to a point where evaporation of any remaining moisture and drying of the sample begins to occur;
- An evaporation front progressively penetrates the material, drying as it proceeds;
- A first stage thermal decomposition occurs at the surface of the material as devolatilisation reactions occur that release gas and begin the formation of char, creating a 'pyrolysing zone';
- Tars, water vapour and evolved gases pass through the char, causing secondary reactions to occur either through the cracking of heavier volatiles or due to exothermic gasification and combustion of the char.

Mohan et al., 2006 provides an alternative explanation that describes the primary breakdown of the solid material and evolution of volatile matter, as overlapping secondary reactions commence. This leads to a complex cycle of dehydration and reformation, phase changes and molecular synthesis, all of which are impacted by processing parameters such as residence time, heating rate and temperature. The ultimate result of pyrolysis processing of biomass is that it achieves a thermochemical decomposition of the material into three primary fractions – biogas, bio-oil and biochar:

2.9.1 Biogas

Pyrolysis biogas produced from biomass is a mixture of volatile gases that evolve at different temperatures and at different rates, depending on input feedstock composition (Shafizadeh, 1982). Primary gases that evolve during thermal decomposition include carbon dioxide (CO_2), carbon monoxide (CO), hydrogen (H_2), methane (CH_4) and other hydrocarbons. The main source of weight loss, correlated with temperature and time using thermogravimetric analysis (TGA), typically occurs due to the evolution of CO_2 and CO, while predominance of volatile gases of higher calorific value such as CH_4 and H_2, tend to appear at moderate (380-450˚C) and high (above 550˚C) temperature intervals as decomposition and recombination reactions advance (Strezov & Evans, 2009).

2.9.2 Bio-oil

Pyrolysis-derived bio-oil is a highly oxygenated, complex mixture of compounds presented as a dark brown liquid that also includes a percentage of water. The moisture content of any given material feedstock run through a dry pyrolysis process is also a major factor in the formation of acidic compounds in the bio-oils and can significantly impact on process kinetics and reactions (Demirbas, 2004). In order to minimise the risk of complications during the conversion process, a dry feedstock of ideally <10% moisture is required, though as previously outlined, this can require a considerable amount of energy and capital intensity to achieve.

Chemically, bio-oil includes an assortment of acids, esters, pyrones, aldehydes, sugars, phenolics and other compounds, the molecular weight distribution of which is partially dependent on reaction parameters, as well as the particle size and type of feedstock (Mohan et al., 2006). The oxygen content of bio-oil is typically around 35-40% of the liquid and together with its highly acidic nature, are major differentiating features that combine to reduce the energy content of this product as a fuel and make it highly unstable and often corrosive (Czernik & Bridgwater, 2004).

While bio-oil can be burnt directly as a fuel in modified combustion engines (Chiaramonti et al., 2007), upgrade of pyrolysis liquids to a more energy dense, valuable ‘green crude’ commodity is also possible (2011b). Upgrading involves a process of deoxygenation to address the inherent instability of bio-oil and there are several methods that have been trialled to produce either hydrogen or hydrocarbons, including steam reformation, hydrogenation and catalysis (Wang et al., 1997; Zhang et al., 2005; Demirbas, 2009; Steele et al., 2009; Wang et al., 2010).

2.9.3 Biochar

Otherwise referred to as ‘char’ or ‘charcoal’, biochar is essentially what remains of the biomass material after the highly volatile matter has been driven off with temperature, typically when heating is limited to 550^{o}C. Biochar

is comprised of a carbon matrix of very high surface area and it also contains the minerals and many of the nutrients that remain from the growth cycle of the biomass (Antal & Grønli, 2003). Certain types of biochar that contain low ash content can be used as an effective metallurgical coking coal replacement and indeed wood charcoal was historically used for such applications (Rehder, 1994).

Notably, of all the biomass processing options outlined in the previous section, pyrolysis is one of the only means to synthesise char, in addition to producing liquid transport fuel substitutes and biogas. The char product is potentially significant and is gaining acceptance as a useful soil conditioner (Lehmann et al., 2006; Liang et al., 2006; Chan et al., 2007). It is also regarded as one of the only viable means to draw down large volumes of CO_2 from the atmosphere (via photosynthesis of biomass) and to lock it safely and relatively stably into soil – an effective means to achieve biological carbon capture and sequestration or 'bio-CCS' (Lehmann & Joseph, 2009). This differs from conventional biomass cultivation and greenhouse gas 'offset schemes' in that the chemical structure and stability of the char produced by slow pyrolysis can ensure a carbon half-life and residence time in soil of hundreds to many thousands of years, as opposed to returning to the atmosphere in a short time frame as CO_2, following biological decomposition of the dead organic matter (Verheijen, 2010).

In general terms, pyrolysis processing parameters can be varied to drive towards prioritisation of either bio-oil or biochar production, the difference between which is dependent on the heating rate, maximum temperature threshold, reactor design and residence time (Yaman, 2004; Goyal et al., 2008). Maximum bio-oil production is achieved through fast or 'flash' pyrolysis, in which biomass is heated to temperatures of up to 650°C, typically with a short residence time of less than 1 second (Bridgwater & Cottam, 1992). Slow pyrolysis, by contrast, drives towards production of an increased proportion of char and employs slow heating rates (10-20°C/min), with commensurately long residence times taken to a temperature ceiling of no more than 550°C (Williams & Besler, 1996).

Specific heats of reaction as they occur at different points in the heating process can be measured at a micro scale and reveal the nature of the thermal decomposition taking place within any given material as temperature increases (Strezov et al., 2003a). This can be correlated with incremental changes in temperature over time to ascertain whether endothermic or exothermic reactions are occurring, thereby providing an understanding of the process energy inputs required to achieve thermal breakdown of the feedstock. The technique designed for this specific purpose, known as Computer-Aided Thermal Analysis (CATA), is established in the literature (Strezov et al., 2004) and summarised as follows.

CATA firstly involves packing a biomass sample to a density of 400 kg/m^3 inside a glass tube that is insulated by alumina ceramics. Prior to commencement, carbon soot is laid on the exterior of the glass cylinder to ensure uniform distribution of heat throughout the sample and the entire array is inserted into the centre of a graphite heating element, as shown in Figure 8 below. The assembly is next placed inside an infrared furnace and both the heating element and the sample kept under inert atmosphere with separate flows of argon gas. Using the flow of the carrier gas, a positive pressure is maintained across the sample to ensure that the volatiles generated by the decomposition process are promptly removed from the heated zone.

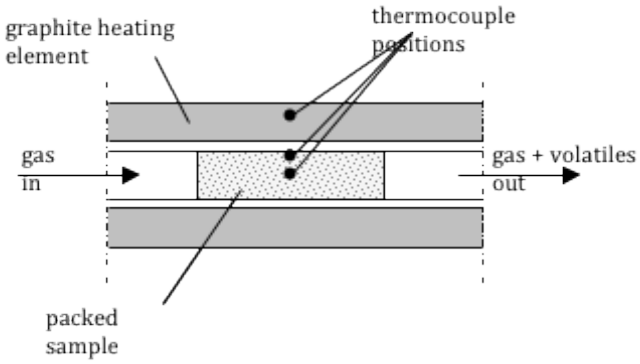


Figure 8. Diagram of the CATA experimental set-up as per Strezov et al., 2004

Three chromel-alumel (K type) thermocouples are used during the measurements, one embedded inside the graphite tube as part of the control loop for maintaining the heating rate of the furnace at 10^{o}C/min and two thermocouples placed on the surface and in the centre of the sample. The temperatures are then logged as a function of time at 1 Hz and the resulting data stored in a computer. The data is then manipulated to provide a consolidated thermal analysis by employing a numerical approximation of the heat conduction equation (1) based on the following inverse thermal modelling relationship:

$$\rho \mathrm{Cp} \frac{\partial \mathrm{T}}{\partial \mathrm{t}} = \mathrm{k} \frac{\partial}{\partial \mathrm{r}} \left(r \frac{\partial T}{\partial r} \right) \qquad \textit{Equation (1)}$$

The sample is first numerically divided into a number of nodes (*n*) across the radius. For each node an estimate is made based on the heat balance principle (i.e. heat accumulated in the node is equal to the difference between the incoming and outgoing thermal energies). The boundary conditions of the system are that the temperatures measured at the centre and surface of the sample, and the heat flux calculated assumes that the heat transfer from the graphite to the sample was achieved by radiation according to equation (2):

$$Q = F_{1-2} \sigma \left(T_g^{\,4} - T_s^{\,4} \right) \qquad \textit{Equation (2)}$$

The radiation shape factor $F_{1\text{-}2}$ which is a function of the emissivity of both glass and graphite tubes, as well as their surface areas, has previously been determined through calibration (Strezov et al., 2000). On this basis, a computational matrix is thus generated using equation (3) to estimate the volumetric specific heat of the heated sample.

$$\rho C_p = \frac{2\pi n \Delta x Q_{(t)}}{\frac{\Delta x^2 \pi}{4\Delta t}\left(T_0^t - T_0^{t-1}\right) + \frac{\Delta x^2 \pi}{\Delta t}\left(n - \frac{1}{4}\right)\left(T_n^t - T_n^{t-1}\right) + \sum_{i=1}^{n-1} \frac{2\pi \Delta x^2 i}{\Delta t}\left(T_i^t - T_i^{t-1}\right)}$$

Equation (3)

The volumetric specific heat estimated by equation (3) has apparent values, which means that the heats evolved during decomposition (ΔH) of the heated sample are included in the specific heat data ($Cp = Cp^{*} + \Delta H/\Delta T$). Overall, this technique has been tested on a range of calorimetric calibration materials and the accuracy of the method found to be approximately in the order of $\pm 2\%$ (Strezov et al., 2003a).

The inherent properties of the input feedstock to pyrolysis have a considerable influence on the outcome of a thermochemical conversion process. Table 4 provides a series of examples of different forms of biomass and their biochemical composition. From this brief review of biomass sources and types based on the delineation put forward by McKendry 2002a (with the addition of residues and wastes), it can be seen that the fundamental chemical properties of different types of biomass differ markedly both within and without these sub-classifications. As a general rule, woody biomass tends to be very low in ash content (mineral matter) and high in volatile matter. Aquatic plant biomass is quite diverse and properties differ between freshwater and saltwater species, the latter being particularly high in ash content with up to over one-third by weight being registered (36.4%).

The relationship between hydrogen, carbon and oxygen, drawn from a proximate analysis, is well understood and this can be directly correlated to the high heating value (HHV) of any plant biomass material (Demirbas, 1997; Sheng & Azevedo, 2005). Moreover, the ratio of these elements is further reflected in the relative concentration of carbohydrates, proteins and lipids, the former of which is especially prominent in terrestrial plants that require a high degree of structural rigidity such as lignin in woody biomass (Balat, 2008). Since the heat of formation of carbohydrates is approximately one third of hydrocarbons and lipids, this theoretically means that the energy density of plants lower in carbohydrates and higher in protein and lipid content makes them more suitable to thermochemical conversion and therefore hydrocarbon production, such as in relation to algae (Ginzburg, 1993; Miao et al., 2004).

Modern slow pyrolysis reactors are purpose designed to maximise the formation of char using slow heating rates and long residence times and there are a number of known designs of slow pyrolysis reactor in operation. The first uses an ablative pyrolysis technique whereby the feedstock is mechanically pressed and moved over a heated surface, partially melting it to leave an oil film that then evaporates leaving behind a charred residue (Balat, 2008). The second type uses a fluidised bed, which uses a mixture of conversion and conduction to systematically heat the material as it passes through the reactor (Zabaniotou & Karabelas, 1999). A third option is vacuum pyrolysis wherein a low-pressure environment contains the reaction, from which a char is ejected through a pressurised seal on a moving conveyor (Mulligan et al., 2009). Finally, the most common design involves a heated kiln in which biomass is either fed using an auger, agitated with a sweeper or mixed using a rotational drum to achieve slow thermochemical decomposition as temperature is slowly increased (Lehmann & Joseph, 2009).

2.10 Pyrolysis of microalgae

Previous work investigating the pyrolysis of microalgae has tended to focus on the fast processing route to maximise production of bio-oil for refinement into liquid fuels (Miao et al., 2004; Demirbas, 2006). One study found that the fast pyrolysis of *Chlorella protethcoides* and *Microcystis aeruginosa* produced a bio-oil with a considerably higher average HHV of 29MJ/kg than that produced from wood (Miao et al., 2004). TGA has been used in several studies as a means to better understand the thermal degradation behaviour of several species of microalgae, including the marine alga *Dunaliella tertiolecta* (Zou et al., 2010) and the freshwater *Chlorella protethcoides* and *Spirulina platensis* (Peng et al., 2001). This work demonstrated that the maximum peak of devolatilisation in microalgae shifts to higher temperatures, as the heating rate increases.

The marine coccolithophores, *Emiliana huxleyi* and *Gephyrocapsa oceanica*, were subjected to pyrolysis at a range of different temperature thresholds up to 500℃, for a period of 100 hours (Wu et al., 1999b). This led to the evolution

of a large proportion of hydrocarbons, most pronounced at the optimum temperature of 300℃, which was associated with the large proportion of lipids, fatty acids, alkenone and alkenoate found in the raw material. A novel approach extracted natural lipid from the green microalgae *Nannochloropsis* sp. using organic solvents prior to transesterification into biodiesel, while the residue was subsequently pyrolysed (Pan et al., 2010). This residue was found to devolatilise at a substantially lower temperature than ligno-cellulosic feedstocks, due to the absence of structural reinforcement of the biomass and demonstrates the viability of a 2-step separation process that can maximise value and liquid oil yield.

The slow pyrolysis of microalgae presents an opportunity to combine a highly productive form of biomass, well suited to thermochemical breakdown, with a technology to produce renewable oil and gas, in addition to a bio-CCS product that can reduce the greenhouse gas intensity of point-source emissions (and thereby reduce atmospheric CO_2 concentration). Combining microalgae production with pyrolysis processing is recognised as a sustainable development opportunity (Demirbas, 2011), however to date the prospect of maximising char with a view to bio-CCS has only been reported in relation to macroalgae (Bird et al., 2011). A critical consideration is whether or not the combined impact of the microalgae cultivation and pyrolysis processing value chain is able to deliver a net benefit in terms of carbon abatement and other indicators of environmental impact, since this is a fundamental premise of the opportunity. As such, the application of life cycle assessment (LCA) techniques is critical in order to estimate the likely impact of this proposition, at an industrial scale.

Table 4. Proximate and Ultimate Analysis Data from a Selection of Biomass Samples

	Biomass Types (McKendry, 2002a)				
	Woody plants	Herbaceous plants/grasses	Manures	Aquatic Plants	Other residues & wastes
Citations	(McKendry, 2002a; Strezov et al., 2003b; Demirbas, 2004; Balat, 2008; Goyal et al., 2008)	(Ghetti et al., 1996; McKendry, 2002a; Onay & Kockar, 2003; Strezov et al., 2008)	(Hossain et al., 2009; Ro et al., 2010; Xiu et al., 2010; Cantrell et al., 2012)	(Miao et al., 2004; Ross et al., 2008; Bae et al., 2011; Li et al., 2010; Muradov et al., 2010)	(Karaosmanoglu et al., 1999; McKendry, 2002a; Oasmaa et al., 2003; Demirbas, 2004; Putun et al., 2007; Yanik et al., 2007; Strezov & Evans, 2009)
Sample Biomass Sources	Radiata pine; Fir; Danish pine; Willow; Poplar; Spruce	Linseed; *Miscanthus;* Switchgrass; *Sorghum; Triticum; Hibiscus; Cyanara; Arundo; Pennisetum*	Sewerage sludge; chicken litter; swine solids; dairy; paved feedlot; turkey litter	*Dunaliella; Chlorella; Microcystis; Laminaria; Undaria; Sargassum; Lemna minor; Fucus; Chorda*	Tobacco residue; olive kernel; rapeseed straw/stalk; forestry waste; corn cob; oreganum stalk; wheat straw; hazelnut shell; paper sludge

	Woody plants	Herbaceous plants/grasses	Manures	Aquatic Plants	Other residues & wastes
Ash/%	<1.0	0.7-20.1	14.8-81.8	5.8-36.4	1.4-11.2
Volatile Matter/%	82-86.3	63.1-81.7	10-80.7	37.1-54.6	60.0-75.5
Fixed Carbon/%	13.4-17	7.9-17.9	1.9-25.4	8.3-39.6	13.4-30.2
Carbon/%	20.3-52.2	32.9-62.1	16.2-47.3	21.5-62.0	27.5-51.6
Hydrogen/%	2.4-6.3	4.8-9.1	0.5-6.1	4.1-8.8	3.9-8.5
Nitrogen/%	<0.2	0.2-3.9	1.8-4.6	0.9-9.8	0.4-2.0
Oxygen/%	16.5-41.5	24.9-59.3	20.1-57.5	19.4-57.0	22.9-53.0
Total Sulphur/%	<0.1	<0.3	<1.0	0.6-2.4	<1.9

2.11 Life cycle Assessment

2.11.1 Introduction

LCA is a tool within the broad discipline of life cycle management (LCM), “a business management approach that can be used by all types of businesses (and other organisations) to improve their products and thus the sustainability performance of their companies and associated value chains” (2009). LCA is commonly used as a means to benchmark and compare designs, processes and systems, with a view to continuous improvement. Based on standardised methods published by the International Standards Organisation (ISO 14040/14044 [2006]), it can provide valuable insight into the overall efficiency and impact of discrete energy and material flows that are relevant to processing and manufacture of a given product across its various life cycle stages, and for assessing the aggregated impact of these as a whole.

The benefits of conducting a LCA include the ability to:

- identify and thereby concentrate efforts on specific environmental and economic risks, or ‘hotspots’ within a product life cycle
- gain an understanding of both the upstream and downstream implications of various system or product design choices
- inform and guide decision-making as part of an innovation program
- communicate more effectively and credibly regarding environmental claims
- benchmark, report and track on progress over time
- apply a common life cycle impact assessment (LCIA) method to effectively compare the overall product, system or process ‘footprint’ with its relevant alternatives or incumbents

A common criticism of LCA studies based on the last point above, including those relating to biofuels, is that they often have no collective basis for real comparison of results and are typically not based on a shared set of assumptions or assessment methods (Davis et al., 2009; Miller, 2010). As such, LCAs are sometimes criticised of

being manipulated to justify environmental claims, or to retrospectively produce favourable or biased results of products. Likewise, many published LCA studies often present little more than an energy and greenhouse gas (GHG) audit, or life cycle inventory (LCI) only, with no impact assessment methodology applied at all. As such, the relative impact of various identified or documented flows of energy or materials at a macro-scale can be either absent, obscured or misrepresented, even where large flows for instance may be immaterial to the overall outcome (or vice-versa).

While this section presents a selection of published LCA studies relating to microalgae biofuels, it is not the intention of this review to query specific numbers or findings, as such, or to comment on the veracity of results. The purpose of reviewing existing studies is to underscore how differences in LCA methodology make it difficult to achieve collective progress towards commercialisation of the microalgae biomass value chain in the absence of shared methods for framing of studies and presentation of relevant data, including assessment of environmental impact. As such, the purpose of this investigation is to highlight the many variables inherent across the microalgae life cycle, from species selection through to processing and delivery of downstream products, with a view to recommending a more strategic, industry-wide collaborative approach to LCA-driven innovation based on agreed standards.

2.11.2 Review of existing microalgae LCA studies

The US Department of Energy published a *National Algal Biofuels Technology Roadmap* under the auspices of the Biomass Program in May 2010 (2010b). This document sets out the broad parameters within which techno-economic assessment and innovation of the algae biofuel product value chain can and should occur, in order to drive towards full commercialisation. It advocates the integration of recognised LCA methods, with a specific focus on leveraging previous biofuel feedstock studies. Additional aspects considered in the DOE report include the opportunity to leverage GIS technology to identify specific areas suitable for scalable microalgae cultivation, based on availability of non-arable land and proximity to necessary process inputs, infrastructure and markets. The report also reflects on co-location with synergistic industries, such as stationary

power generators or wastewater treatment plants, as a means to explore innovation in the sector.

The DOE roadmap provides a conceptual framework that highlights the importance of LCA as tool that can contribute to commercialisation efforts. Notably, the report also observes that in addition to measuring net greenhouse gas emissions, LCA “can also assess impacts and trade-offs associated with utilisation intensity for water, energy, nutrients, and other resources” (2010b). Overall, the roadmap presents a critical challenge for LCA, namely that there are multiple cultivation and processing choices that can be made, spanning species selection, cultivation, intermediate constituents, conversion processes and end-user products and markets. The inference being that without at least some degree of harmonisation of data collection, boundary definition and/or assessment methods, effective comparison, prioritisation and innovation across multiple pathways will be difficult.

The existing published microalgae LCAs reviewed here are divided into three broad categories. The first covers the spectrum from energy, greenhouse gas and mass balance calculations, to high-level ‘scoping’ LCA studies (Batan et al., 2010; Pfromm et al., 2011; Yang et al., 2011). These do not report beyond a limited set of metrics and/or do not appear to apply or present any discrete LCIA method.

The second category of studies appear to be based on conventional LCA reporting practices that take a more comprehensive approach to LCIA (Kadam, 2002; Lardon et al., 2009; Collet et al., 2011; Soratana & Landis, 2011). Nevertheless, they do not generally share a common set of goals, system boundaries, assumptions and/or impact assessment methods, and only the overall approach and structure each adopts is similar, at the very highest level (as proscribed by the ISO standard).

The final category sees LCA results and ‘life cycle thinking’ either directly or indirectly implicated through techno-economic assessments (TEAs), that seek to primarily address the commercial feasibility of the process overall (Beer et al., 2008; Chisti, 2008). These may or may not include an approach designed to also measure, assess and report on

environmental impacts, however their consideration is necessary to appreciate the growing body of work in this area. While a TEA is a fundamentally different proposition to an LCA, it must be based on relevant assumptions of productivity, as well as material and energy flows, that enable a fully costed model to be assembled. As such they do share common data elements with LCA, although the approach to data collection, interpretation and validation may well be quite different.

Since microalgae is posited as a sustainable alternative to fossil sources of material and energy, those concerned primarily with assessing the environmental impact of industrial microalgae production seek at a minimum to ensure that the overall value chain leads to a net carbon reduction (Clarens et al., 2010; Demirbas, 2011; Pittman et al., 2011). Those interested in techno-economic studies seek, in the main, to establish the capital and/or operating cost profile of an end-to-end process, to ensure economic viability of the proposition. Ultimately, integrated assessment from both perspectives is necessary in order to realise the goal of a scalable, ecologically sound, socially responsible and yet commercially viable solution, surely the intent of sustainable development (Benemann, 1997; Patil et al., 2008; Wang et al., 2008; Brennan & Owende, 2010; Demirbas, 2011).

However, reducing capital and operating costs, and adequately assessing environmental impact is complex as fully scaled commercial operations are essentially non-existent and laboratory findings must often be relied upon for extrapolation (Lardon et al., 2009). Cultivation and harvesting technologies for instance are mostly immature and yet to be realised at scale, hence many studies represent, “a prospective LCA of a non-existing process” (Collet et al., 2011), and very few published studies have even gone on to consider human resource demands of operation, such as labour implications (Campbell et al., 2011).

One study sought to overcome the nascent status of a scaled microalgae industry by suggesting a bulk growth model that notionally enables more accurate LCA studies to be formulated (Quinn et al., 2011). This uses a series of mathematical models relating to light intensity, nutrient uptake and lipid accumulation for instance, to predict maximum thresholds of productivity, also applying a sensitivity analysis to develop a level of

confidence in results. The approach put forward also makes allowance for differing geographic locations, since this impacts directly on growth and is a key aspect often overlooked in existing microalgae LCA studies. Comparability of algae LCA studies also depends greatly on consideration of a common species, since a biochemical profile is fundamental to achieving productivity goals and downstream refinement into desired end products (Scott et al., 2010).

Critical differences between LCA and TEA studies create challenges in constructing an integrated picture since they each have slightly different conventions and overall orientation. In an LCA, it is common to specifically *exclude* the impact of fixed assets and infrastructure, since experience has shown that it is the environmental impacts related to the operational phase of a product value chain or process that dwarf all else. On the other hand, a financial assessment seeks to encompass all assets and operational costs (including labor), as accurate capital and operating projections are fundamental to building a business case, raising project finance and to calculating tax benefits such as depreciation. In this way, the veracity of LCA data is often far less 'complete' in terms of the precision of actual numbers than the 'line-by-line' accounting approach taken by a TEA. Nevertheless, sensitivity analysis, coupled with LCIA, can reveal credible scientific insights based on LCI results, without the need for absolute certainty on the volume of individual flows, especially where their variance is found to be inconsequential to the final result.

The existing body of work designed to assess the industrial-scale microalgae prospect seeks to compare and contrast findings from a diverse number of analytical viewpoints (Table 5). For instance, some reports use the intermediary or end products (e.g. FAME, carbon abatement, MJ equivalent) as the unit of comparison (Batan et al., 2010), whereas others use the cultivation system (Chisti, 2008), or perhaps both (Agrawal & Singh, 2009). There are several factors to be considered in design of a cultivation system, though it can be generalised that the greater amount spent on capital equipment and infrastructure (such as when comparing closed photobioreactors with open pond systems), the higher the biomass productivity per unit area that can be expected (Benemann, 1997; Clarens et al., 2010; Jorquera et al., 2010; Kumar et al., 2010;

Demirbas, 2011). Hence, a key position many studies attempt to establish is the point at which this trade-off (cost versus productivity) is no longer justified.

The comparison of studies highlights the fundamental differences in approach to system boundary definition (Table 5). All of these positions are equally valid however contribute to general confusion regarding inclusions or exclusions, goals, functional units, impact reporting categories and/or methods that would otherwise make fair and transparent, 'level playing field' comparison of value chain options across the innovation landscape possible (Batan et al., 2010).

2.11.3 Functional units, comparability, inclusions and exclusions

A study comparing the life cycle impact of cultivating microalgae in open ponds versus photo bioreactors (PBR) proposes a focus on net energy ratio (NER) as a functional unit, wherein the construction process and materials used, in addition to process energy, are collectively taken into account when making inferences about their relative suitability and efficiency (Jorquera et al., 2010). However, the environmental impact of their respective operational lives, in this case mostly related to the energy used in pumping, mixing and CO_2 delivery, as well as possible impacts associated with process nutrients, will far outweigh these calculations relating to infrastructure (Kadam, 2002), hence this metric appears questionable.

Another illustrative work targets LCA of algae biodiesel specifically, suggesting through this lens that for every 1kg of algal biodiesel produced, approximately 1.4kg of co-products are generated (Sander & Murthy, 2010). This study is notable for several reasons. Firstly, it adopts the RMEE method wherein data relating to specific unit processes is assembled *prior* to the selection of system boundaries with the intent of avoiding arbitrary exclusion of certain items. The functional unit chosen relates to 1000 MJ of energy, based on a 'well-to-pump' system boundary. Mass, energy and economic value ratios are calculated for each input, with a cut-off ratio of 5% chosen as the sole basis to exclude items. This has the effect of neglecting the imbalance that often exists in relation to the type and volume of certain flows hence applying a sensitivity filter *before* any impact characterisation is undertaken carries a risk of distortion. That is, the

environmental impact of certain industrial chemicals for instance are often disproportionate to the volume of their flows, hence this LCA approach could overlook such inventory items that would otherwise be captured under the terms of a more complete study.

Another ‘problem oriented’ study coupled wastewater treatment and ‘high-rate’ algal ponds together to solve both an environmental and commercial problem. This is proposed as an example of the means to close the competitive price gap between the cost of biofuel production and incumbent fossil fuels (Park et al., 2011). In addition to removing nutrient from the water (a useful process input for algae growth), the capital and operating cost of a conventional wastewater treatment plant can be redirected to algae ponds and process water is better utilised overall.

Of particular relevance to realising full-scale commercialization of algae biomass, biofuels and bioproducts is the establishment of a ‘level playing field’ approach to synthesis and interpretation of LCI results, that enable them to be interpreted in a meaningful way. This is essential in order for such studies to be comparable across the industry itself, regardless of the desired output product/s (Singh & Olsen, 2011).

A comparative study of microalgae systems modeled 20 different cultivation scenarios, with a view to evaluation of 3 key parameters, namely, chosen material for PBR construction, source of nutrients and source of CO_2 (Soratana & Landis, 2011). A further temporal dimension was added to this analysis to view the impacts of various scenarios in terms of length of operation of 3 alternate timescales. The LCIA method used here was based on the Tool for the Reduction and Assessment of Chemical and other Environmental Impacts (TRACI), from which nine impact reporting categories were selected and reported against. The functional unit in this case benchmarks all LCIA results against the ability of a standardised PBR design to deliver a calculated yield of algae biomass over time (essentially based on productivity potential), with a view to downstream conversion to biodiesel. The standardisation of reactor design in this work

Table 5. Comparison of Microalgae LCA System Studies

Study		Features of the study			
		Goal & Scope/ Product Orientation	***System Boundaries***	***Functional Unit***	***LCIA/ Reporting Method***
1	(Batan et al., 2010)	Net energy ratio & GHG of PBR grown *Nannochloropsis* biodiesel + co-products	Cultivation-to-consumer; "Strain-to-pump" cf. "well-to-wheel"	Temporal, based on production process over 1 year	GREET 1.8c; displacement of co-products applied
2	(Campbell et al., 2009)	GHG balance of *D. tertiolecta* in open ponds cf. ULS diesel + economic costs; includes people	Pond vs. well-to-tailpipe	$CO_{2\text{-}e}$ of GHG emissions/t/km in an articulated truck	UNFCCC GWPs of GHGs only (100yr)
3	(Chisti, 2008)	GHG ratio of 1.83:1, based on *P. tricornutum* PBR for elect. & biodiesel cf. bioethanol; incl. economic costs	Cultivation to oil extraction + power generation	MJ/t algal biomass	GHG balance only
4	(Collet et al., 2011)	Biogas production cf. biodiesel from *C. vulgaris* grown in open ponds	Cultivation-to-generator gate; includes 30yrs fixed infrastructure	1 MJ fuel combusted in a gas engine	CML; substitution of co-products applied
5	(Clarens et al., 2010)	Producing energy from algae biomass vs. corn, canola and switchgrass	Cultivation-to-processing gate (delivery of biomass)	317 GJ of biomass-derived energy	Crystal Ball; MJ, m^3 H_2O, $CO_{2\text{-}e}$, kg PO_4-eq., Ha land
6	(Jorquera et	Net Energy ratio (NER) of	Cultivation-to-	1kt of dry weight	NER only

	al., 2010)	*Nannochloropsis* sp. grown in multiple growth systems	processing gate (delivery of biomass)		
7	(Lardon et al., 2009)	Expanded boundaries to ascertain broad impact of *C. vulgaris* biodiesel in open ponds cf. diesel	Cradle-to-combustion (fuel), Cradle-to-grave (facility); includes 30yrs fixed infrastructure	1 MJ fuel combusted in a diesel engine	Partial CML: AbD, Ac, Eu, GWP, Ozone, HumTox, MarTox, Land, Rad & Photo
8	(Pfromm et al., 2011)	Mass balance orientation based on chemical engineering tehcniques, held as distinct from LCA 'accounting'	Uses conservation of mass, hence cradle-to-grave, incl. the atmosphere	LHV equivalent of 50m gal of petro-diesel	Balance calculation only - electrical energy, thermal energy, fertilizer, CO_2
9	(Sander & Murthy, 2010)	Benchmarking algae biodiesel against other transport fuels, highlighting sustainability concerns	Cultivation-to-consumer; ("well-to-pump"), 5% cut-off value	1,000 MJ of energy	Relative mass, energy and economic (RMEE)
10	(Soratana & Landis, 2011)	Biodiesel from *C. vulgaris* grown in a PBR, using 3 parameters: PBR material, source of CO_2, source of nutrients	Cultivation-to-pump; temporal also (5,10, 20yrs), includes infrastructure	3650kg of algae, grown over 20yrs	TRACI 3.01
11	(Yang et al., 2011)	Water footprint of open pond culturing of *C. vulgaris*	Cultivation-to-finished product	1kg biodiesel	Water & nutrient balance

provides a useful anchor point, and leads to the observation that choice of PBR material can have a significant impact in relation to several environmental metrics, where this capital infrastructure is included in the model.

Production of algal biodiesel is assessed in a UK-based study, wherein the avoided impacts, or 'reference systems' are also modelled in order to establish the quantum of benefit (Stephenson et al., 2010). LCIA is based here on a recognised, consistent reporting method, EDIP 2003, which adds gravitas and a degree of comparability to the results. In the case of liquid fuel substitutes, extending system boundaries to include combustion is necessary given that in this case, algal biofuel properties will differ when compared directly with their fossil alternatives (Lardon et al., 2009; Kumar et al., 2010).

2.11.4 Co-products and the challenge of impact allocation

Since microalgae systems present an opportunity to bioremediate wastewater streams, address the greenhouse gas emissions intensity of stationary power generators and heavy industry, as well as offset fossil resource consumption, this prospect offers numerous potential environmental advantages when considered from an 'attributional' LCA perspective, albeit from one that addresses multiple problems simultaneously (Clarens et al., 2010). This has important and possibly controversial implications for allocation of environmental impacts and suggests that more of a 'consequential' LCA orientation would neatly sidestep the inherited burden of the upstream processes (such as coal-fired power) that feed into it.

Attributional LCA by definition only really assists with answering a question based on the environmental impact of a burden at any given moment in time, largely based on average production practices. This is useful for simplified benchmarking and certification of environmental performance however fails to recognise the positive flow-on effects that a value-adding solution such as microalgae might deliver over time. Consequential LCA takes on a much larger scope by effectively trying to model scenarios over decades, including coupled flow-on effects and marginal changes, however adds significant additional complexity to the process.

Some published algae LCA studies that take an attributional approach conclude that algal biofuels are likely to perform poorly when compared with terrestrial biofuels from an environmental perspective. This is mainly reflected in the results for CO_2 and nutrients, hence the clear preference towards wastewater and emissions intensive-coupled growth systems as drivers of industrial microalgae commercialisation (Clarens et al., 2010; Pittman et al., 2011; Singh et al., 2011). Further, since water is also identified as a critical limiting factor for many potential algae cultivation sites, exploitation of wastewater for growth of freshwater algae species is likely to be essential to achieve any significant scale of production (Pate et al., 2011).

A thoughtful discussion of allocation methods in a study of algal biodiesel suggests direct substitution (consequential allocation) as the preferred approach (Stephenson et al., 2010), before concluding that by-products and their impacts (where they only substitute existing waste by-products of other processes, such as heat) should be avoided. The reflection is that economic allocation is the simplest and best method to apply, in this case an approach to LCA that is in line with the demand cycles of the open market, albeit perhaps in conflict with the more optimistic, future-oriented view that a consequential orientation would deliver, in terms of assessing long terms impacts related to sustainable development.

Of critical interest to allocation in the microalgae context is the extent to which the downstream cultivation of microalgae (where CO_2 from an adjacent power station is utilised for growth) is considered an inherited environmental burden to the overall process. An undesirable outcome may result through application of an attributional LCA method, where burden is passed on and distributed proportionately down a value chain, whereas a consequential approach may lead to a more favourable assessment over time.

2.12 Conclusion

The sustainable cultivation of biomass as a strategic response to climate change and dwindling fossil oil supplies is promising, albeit faces many challenges. As global population and therefore food demand continues to rise, it is difficult to see how

dedicated, '1st generation' biofuel or biomass crops can be justified, where they are produced on arable land. Notwithstanding this, the decline of existing farmland through climate change impacts such as desertification, drought and salinity also places pressure on food production and this is highly likely to continue and possibly worsen in coming decades. Expansion of agriculture in tropical countries through widespread land clearing practices likewise creates its own environmental and socio-political conflicts. Furthermore, a growing middle class in populous regions of the world, such as Asia and Latin America, demands ever-increasing levels of animal protein in their diet, which assumes a greater intensity of all agricultural inputs, including lower trophic level plants and food commodities that add to a concentration of environmental impacts and demand for agricultural outputs.

The scalable culturing of microalgae, with all of its contingent technical and commercial challenges, offers a possible means to avert many of these issues, while simultaneously fixing large quantities of carbon via photosynthesis from either the atmosphere or directly from point source carbon emitters. The literature demonstrates that cultivation can also be achieved while bioremediating wastewater streams that often carry high levels of nutrient required for supporting the healthy growth of algae biomass. However, viable production of microalgae biomass at scale remains only a concept and is yet to be successfully demonstrated in practice, though there are precedents in the nutriceutical industry and emerging pilot-scale research and commercial projects around the world that suggest this may yet be possible.

Pyrolysis processing, with an emphasis on slow heating rates and a long residence time that pushes the thermal decomposition process of biomass towards maximum char production, provides a means to produce a soil amendment and carbon abatement product, in addition to bio-oil and biogas that can be used for the production of liquid transport fuels, chemicals and electricity. Given the inherent productivity of microalgae and its lack of lingo-cellulosic material, existing studies suggest that as a source of high volume biomass, the pyrolysis processing of this material could offer significant levels of carbon abatement that would notionally also improve the health and general productivity of soil.

While this is an exciting prospect, it is important that this notional production system is placed in the context of the existing studies in the microalgae field and fully assessed to ensure that at a minimum, it produces less greenhouse gas to deliver the biochar and its associated co-products than it ultimately reduces. Beyond the traditional scope of many studies, it is important that broader embodied impacts are also taken into account to ensure that a ‘net benefit’ can be delivered. LCA can be a valuable tool for innovating across the microalgae value chain with a view to full commercialisation. However, there needs to be greater methodological consistency between LCA studies to guide this effort. In the case of algal biomass, allocation is a key methodological issue that needs to be strictly consistent in relation to assessment of all technologies and pathways, as this enables more balanced decision making to be made based on both utilisation of wastes and generation of co-products. Future work should address the issue of harmonisation of agreed system boundaries and LCIA methods, collectively benefitting the industry and enabling it to benchmark and report on multiple value chain options with greater confidence and comparability, based on a ‘level playing field’ approach. This effort should draw on the experience of other industries in establishing a common approach, in particular those that have already developed LCA-driven methods, such as the Building Products Innovation Council (Australia) and The Sustainability Consortium for benchmarking of consumer products.

Chapter 3: Thermal Characterisation of Microalgae under Slow Pyrolysis Conditions

Original manuscript published in Journal of Analytical and Applied Pyrolysis, 2009, 85 (1-2), pp. 118-123, while the unpublished data on bio-oil characterisation are presented in Appendix C.

3.1 Introduction

Biomass offers a unique sustainable innovation pathway with potential for a variety of fossil energy and material feedstock alternatives. In addition to stationary electricity production and material feedstock substitutes for products such as plastics and fertilisers, biomass offers many other attractive opportunities for fossil resource displacement, notably liquid transport biofuels (Walker et al., 2005). However, development of sustainable biomass production systems on an industrial scale faces many challenges (Giampietro & Ulgiati, 1997; Ulgiati, 2001). This includes competition with food production for available arable soils, degradation of biodiverse regions, maintaining a positive life cycle energy balance, overcoming nutrient constraints, land use management and sustainable consumption of freshwater resources.

A high volume, cost-effective industrial solution for production of microalgae has been suggested as a major strategic opportunity for cultivation of supplementary biomass that can address the current drawbacks in supply of biomass for energy conversion (Ginzburg, 1993). Cultivation of aquatic microalgae for this purpose offers very high production rates of biomass per unit area and places no demand on available arable soils.

There are several different biomass conversion processes that can yield high calorific value products. Pyrolysis is a processing technique that can be applied to achieve thermal decomposition of biomass in the absence of oxygen to derive renewable oil, gas and char. The bio-oils produced can potentially be used for direct combustion in energy

generation, or can be upgraded further into bio-diesel and bio-chemicals (Miao & Wu, 2004). Key biomass growth nutrients (N, P, K) are also mostly retained in the char that results from pyrolysis processing, hence this product could act as a fertilizer supplement in agricultural systems. Moreover, adding carbon to the soil as char has been found to significantly improve the quality and productivity of soils and could contribute significantly to carbon abatement (Lehmann et al., 2006).

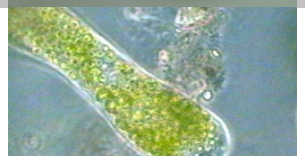
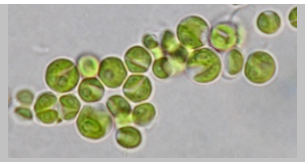
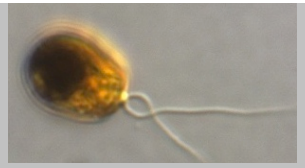
The purpose of this chapter is to evaluate the thermo-chemical properties of six species of microalgae biomass using a slow pyrolysis technique and to form a baseline understanding of their behaviour during thermal decomposition. This aims to reveal if, and what differences exist across a range of microalgae species that present variations in morphology. In particular, application of a novel thermo-analytical technique known as computer aided thermal analysis (CATA) is useful to determine the specific heats of reaction that occur in each sample under unsteady-state heating conditions (Strezov et al., 2003b). This enables derivation of the process energy inputs required to achieve devolatilisation. Of particular interest in this chapter is the capacity of different algae species to produce combustible gases of sufficient quality and quantity to offset the energy requirements of the pyrolysis process.

3.2 Experimental

3.2.1 Materials

Six microalgae species were selected for investigation (Table 6). These represent species either already in commercial cultivation for the production of nutriceutricals and agri-/aquaculture feed, that are otherwise ubiquitous in marine and/or freshwater ecosystems around the world, have high natural lipid yield, high productivity and/or tolerance to environmental factors (salinity, pH, temperature), or that have other inherent characteristics that could offer a commercial advantage. Overall, this selection was made based on species that were accessible, well studied or cultivated and that offer a reasonably broad cross-section of characteristics and behaviour.

Table 6. Introduction to the six species of microalgae examined in this chapter

Species Name		Type	Salt/ Fresh	Morphology
Tetraselmis chui		Green	S	Large cell size; carbohydrate cell wall; highly motile (flagella); 15-30% natural lipid content
Chlorella like		Green	S	Small cell size; tough carbohydrate cell wall & reasonably rigid; high productivity; commercially cultivated as nutriceuticals and animal feed
Chlorella vulgaris		Green	F	Similar to the above however a fresh water species
Chaetocerous muelleri		Diatom	S	Rigid exoskeleton due to Si cell wall; fast-growing; 15-30% oil content; small cell size;
Dunaliella tertiolecta		Green	S	If sunlight too strong, protective coat gives a red/pink appearance; no cell wall; motile
Synechoccocus		Blue-Green	S	Cyanobacteria; high protein content; very small cell size; can form chains or flocculate easily

All species were cultured under controlled conditions at the NSW Department of Primary Industry (Fisheries) laboratory in Port Stephens, wherein temperature, CO_2 enriched air flow (atmospheric air + 2%) and light was controlled. A standard nutrient load (N, P, K & minerals) was introduced to each new volume during cultivation. Bacterial infection during the transfer to progressively higher volume growth vessels was minimised by autoclaving all fittings and volumes, and by prior sterilisation of growth medium (water) with pool chlorine (sodium hypochlorite). This was later counteracted by sodium thiosulphate and finally tested for complete neutralisation prior to addition of the algae culture.

Each of the six species was firstly mechanically harvested by suspended solid centrifuge. The resulting slurry was then transferred to a cream separator to reduce the biomass to a thick paste, prior to initial drying in a conventional oven over an extended period at 50-55°C. All samples were finally ground and dried at 70°C for 3 hours in a vacuum oven prior to pyrolysis in order to remove as much excess moisture as possible.

3.2.2 Thermal analysis

The dried samples were subjected to thermal evaluation to determine their behaviour during pyrolysis. Specific heats of the microalgae samples were determined in-situ using a Computer Aided Thermal Analysis (CATA) technique. Detailed description of the experimental procedure can be found elsewhere (Strezov et al., 2003a). Each sample was packed to occupy a standard volume in the reactor tube and then heated at 10°C/min from a room temperature base until the furnace reached 710°C. Temperatures of the heating element, surface and centre of the packed sample were acquired each second by thermocouple. These temperatures were applied in an inverse numerical model to calculate the specific heat. For the purpose of making calculations, the sample was divided into a grid with an assumed number of nodes across the radius. The heat balance for each node was determined based on the heat conduction principle where heat accumulated by the node equals the difference of input and output heats from the node. The estimated specific heat had apparent values, which means that when an endothermic or exothermic heat of reaction evolved during pyrolysis, the specific heat showed a corresponding increase or decrease in these values. Reported calculations for

the specific heat and energy balance in the current work are based on the initial mass of the sample. Thermal analysis of each sample was repeated twice using this technique in order to confirm the pattern of thermal decomposition.

3.2.3 Gas Chromatographic Analysis of Volatiles

Volatiles that evolved during pyrolysis of microalgae were analysed separately by gas chromatograph. A M200 Micro gas chromatograph from MTI Analytical Instruments was connected to the gas outlet of the glass sample tube. A metallic molecular sieve 5A column (10m in length, 0.32mm diameter) at 90°C was used to separate H_2 and CO while analysis of CO_2, CH_4, C_2H_4, and C_2H_6 was performed on a bonded polymer Poraplot U column (8m in length, 0.32mm diameter) at 55°C. Chromatograms were obtained every 90 seconds using a gas thermal conductivity detector. 'Carrier' helium gas at a rate of 50 ml/min was passed through 100 mg of biomass while maintaining a continuous heating rate of 10°C/min up to the maximum temperature of 750°C. Two reproducible experiments were required in order to confirm the basis of volatile evolution for each algae sample.

3.2.4 Analysis of Bio-oils

The bio-oils produced from pyrolysis of microalgae at 500°C were condensed at room temperature for further analysis. The bio-oils were then dissolved using dichloromethane and subjected to analysis using Matrix Assisted Laser Desorption/Ionization mass spectroscopy (MALDI). The samples were run without matrix under laser desorption conditions with the mass range set between 200 – 5000 amu. The MALDI mass spectroscopy was performed on a Micromass/Waters TOFSPEC 2E time of flight mass spectrometer. The instrument used nitrogen laser of 337 nm with a 4 ns pulse and all spectra were in the positive-ion mode. MALDI was preferred over Size Exclusion Chromatography (SEC) technique for identification of molecular weight distribution due to the inherently complex, heterogeneous character of pyrolysis oils for which there is no common reference standard (Apicella et al., 2003). The detectable mass range was restricted to a maximum of 5000 amu due to the destructive nature of temperature during pyrolysis, whereby larger bio-molecules are unable to survive the thermal decomposition process. Each sample was run twice in order to confirm the distribution of molecules.

3.3 Results and Discussion

Figure 9 shows gas chromatography data of the major volatile products superimposed to the apparent specific heat of algae during slow pyrolysis. All experiments were conducted to a maximum temperature of 750°C, however the main results of interest are those collected at 500°C because industrial pyrolysis processes generally operate at a maximum temperature range of between 450 and 550°C. Specific heats of the selected microalgae species measured at room temperature were in the range of 1.0 – 1.3 MJ/m^{3}K, equivalent to between 1.2 – 2.0 kJ/kgK. At 500°C, specific heat was found to be in the range of 1.4 – 1.7 MJ/m^{3}K.

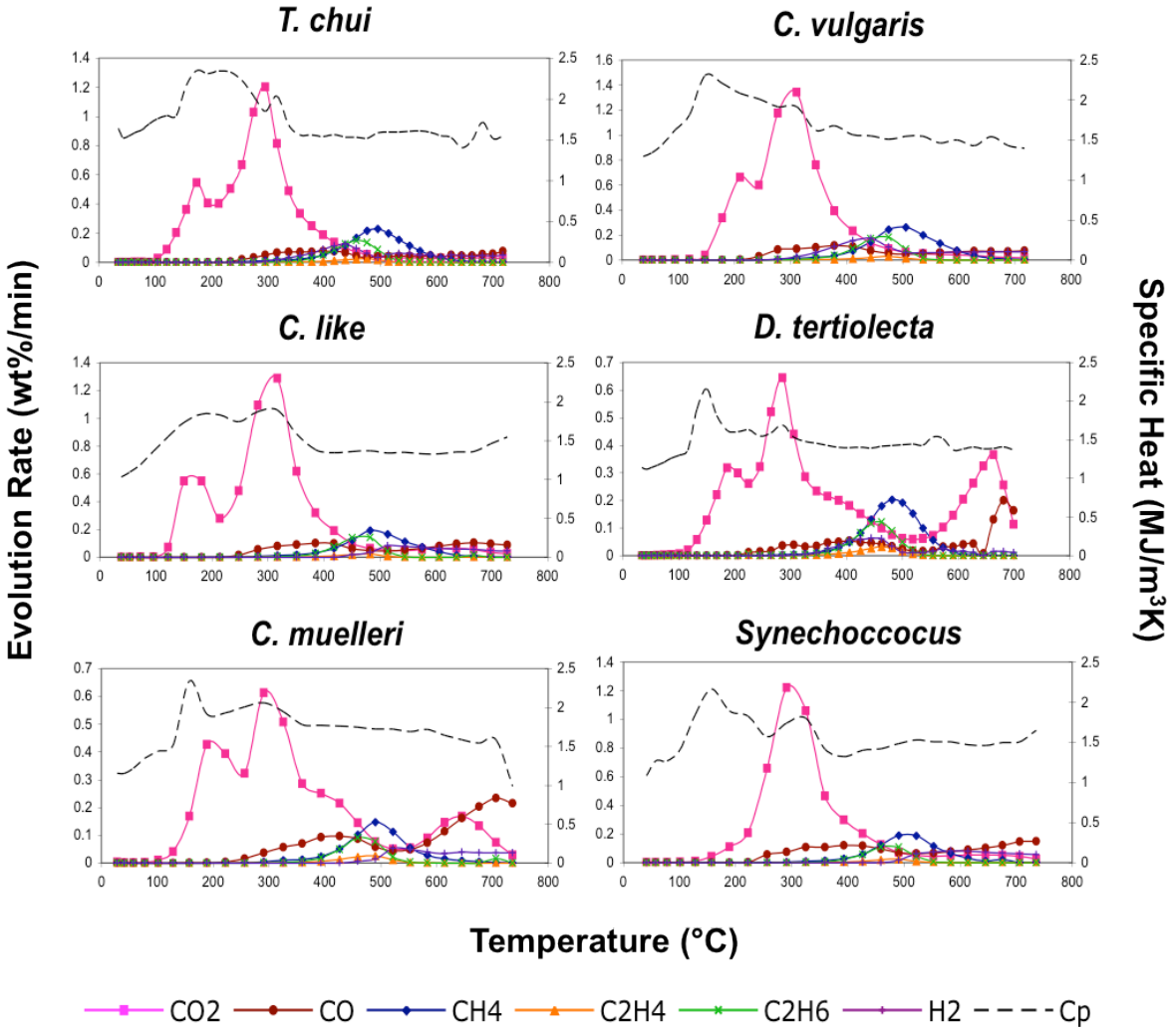


Figure 9. Rate of evolution of volatile compounds from pyrolysis of microalgae superimposed to the apparent specific heat for the heating rate of 10 °C/min

All algae species exhibited a low temperature endothermic peak at between 140-220°C, most likely indicative of the release of strongly bonded hydrated compounds and characterised by elevated levels of CO_2. Following the first endothermic reaction, all species exhibited a second endothermic peak between 250-350^oC, corresponding to the evolution of a significant volume of CO_2. Evolution of CH_4 peaked in all species at around 480-520°C. Likewise, the rate at which CH_4 evolved in this range was approximately the same for all samples. Without exception, C_2H_4 and C_2H_6 evolution preceded the methane peak in all species, commencing at around 450°C. H_2 from *C. vulgaris* and *T. chui* peaked at around 430°C and in *D. tertiolecta* to a lesser extent at 460°C however in the remaining species hydrogen did not start to evolve until between 515-585°C.

The main volatile compound recorded across all species was CO_2, comprising between 10% (*D. tertiolecta*) and 18% (*C. vulgaris*) of total algae weight loss to 500^oC (Table 7). CH_4 release was found to be similar across all species, in the range of 1-2% of dry algae weight. The evolution of C_2H_4 did not vary significantly across species whereas at 500^oC, C_2H_6 began to appear in elevated quantity in *T. chui*, *C. vulgaris* and *C. like*. H_2 evolution from *C. vulgaris* was a clear standout feature of this species, representing 2% of sample weight loss to 500°C. *T. chui* released H_2 within this range also (1.3%) and while *D. tertiolecta* peaked in H_2 production prior to 500^oC, it represented only a small fraction of overall sample weight (0.7%).

Table 7. Volatile gases evolved from microalgae during slow pyrolysis as a percentage of total sample weight at 500°C (%)

Species	**CO_2**	**CO**	**CH_4**	**C_2H_4**	**C_2H_6**	**H_2**
T. chui	14.6	1.3	1.7	0.2	1.3	1.3
C. like	17	1.7	1.4	0.2	1.2	0.2
C. vulgaris	17.5	2.0	1.9	0.3	1.6	2.0
C. muelleri	10.5	1.5	1.0	0.2	0.7	0.1
D. tertiolecta	9	1.0	1.5	0.3	1.0	0.7
Synechoccocus	13.5	2.2	1.2	0.2	0.9	0.1

The energy required to pyrolyse microalgae samples to 500^{o}C as well as the calorific value of the biogas products evolved to this temperature are displayed in Table 8. The total amount of process energy required to achieve thermal decomposition of all species of microalgae is similar at around 1 MJ/kg of dry microalgae biomass. The calorific value of the biogas compounds that could be recovered from each species during decomposition was found to be considerably different between species at 500°C. The theoretical calorific value of the combustible biogas compounds was obtained by converting the accumulated volume of various gases at temperature intervals into energy equivalent based on the known heat of combustion of the respective compounds under stoichiometric combustion conditions.

Table 8. Process energy balance - required energy input (specific heat) relative to calorific value (heat of combustion of volatile gases) during slow pyrolysis of microalgae (MJ/kg of dry algae biomass)

Species	**Processing energy required (MJ/kg) 500°C**	**Calorific value of evolved combustible biogas (MJ/kg) 500°C**
T. chui	1.1	3.4
C. like	0.9	1.8
C. vulgaris	1.0	4.8
C. muelleri	0.9	1.2
D. tertiolecta	1.0	2.4
Synechoccocus	0.9	1.4

In the case of *C. vulgaris*, the total potential energy to be recovered to 500°C was calculated to be 4.8 MJ/kg. At the other end of the scale, *C. muelleri* only released an energy equivalent in biogas of 1.2 MJ/kg. Although only a relatively small amount of combustible gases had evolved from *C. muelleri* and *Synechoccocus* at 500°C, the calorific value of the combustible biogas compounds (under stoichiometric combustion conditions) was still larger than the energy required to heat these microalgae species to 500^{o}C. *C. vulgaris* and *T. chui* produced a similar amount of gas to this temperature, however the calorific value of the volatiles evolved from *C. vulgaris* to this point was

greater due to the presence of larger quantities of H_2 and, to a lesser extent, CH_4, C_2H_6 and CO. Moreover, *C. vulgaris* and *C. like* released a similar amount of combustible gas to 500°C, however this was not of equal heating value being of 1.8MJ/kg and 4.8MJ/kg, respectively. Notably, only a slight increase in processing temperature for *C. like* to 550°C (requiring only an additional 0.1MJ/kg), could lead to an increase in recoverable energy of approximately 1.0MJ/kg. The recovery or heating value of combustible gases from slow pyrolysis of microalgae was found to be lower than other forms of biomass, such as elephant grass (10MJ/kg), rice husk (7.4MJ/kg) or wood (16.7MJ/kg) (Raveendran & Ganesh, 1996; Strezov et al., 2008).

Figure 10 shows the evolution rate of pyrolysis products with temperature, as a percentage of total sample weight. The greatest weight loss for all species was observed during the second stage of algae devolatisation (250-350°C). Unlike higher plants, such as woody biomass that are typically made up of 95% or more hemicellulose, cellulose and/or lignin components, microalgae consist primarily (between 60-80%) of varying ratios of protein, lipid and carbohydrate (Demirbas, 2002). This generally means that notwithstanding differences between microalgae species, they have a tendency to devolatilise at a lower temperature than sources of lignocellulosic biomass (Raveendran & Ganesh, 1996; Peng et al., 2001).

Deriving maximum liquid yield at low temperature is relatively important, as temperatures beyond 500°C may begin to crack the oil fraction. During this experiment, maximum liquid evolved at between 280-320°C, except in D. *tertiolecta* that had two peaks at 245°C and 325°C. The dip in liquid evolution between these two peaks appears to correspond with an elevated production of biogas, at approximately the same temperature at which an endothermic reaction is observed. *T. chui* and *C. muelleri* produced a relatively high ratio of liquid to gas products in this temperature range (approximately 4:1) whereas in other species the ratio of evolved products tended to be lower. In *T. chui* only, there appeared to be a rapid and significant devolatilisation of this sample between 280-320°C. In other microalgae species, gas and liquid products evolved at a slower rate across a broader temperature range of approximately 250°C.

Observation of the ratio of liquid (representing both bio-oils and water), gas and char products across all microalgae species reveals differences in evolved ratios to 500°C (Table 9). Both *Chlorella* species evolved a high proportion of liquids (41%), as did *T. chui* (43%) and *Synechoccocus* (38%). By contrast, *D. tertiolecta* produced only 24% by weight in pyrolysis liquids at 500°C.

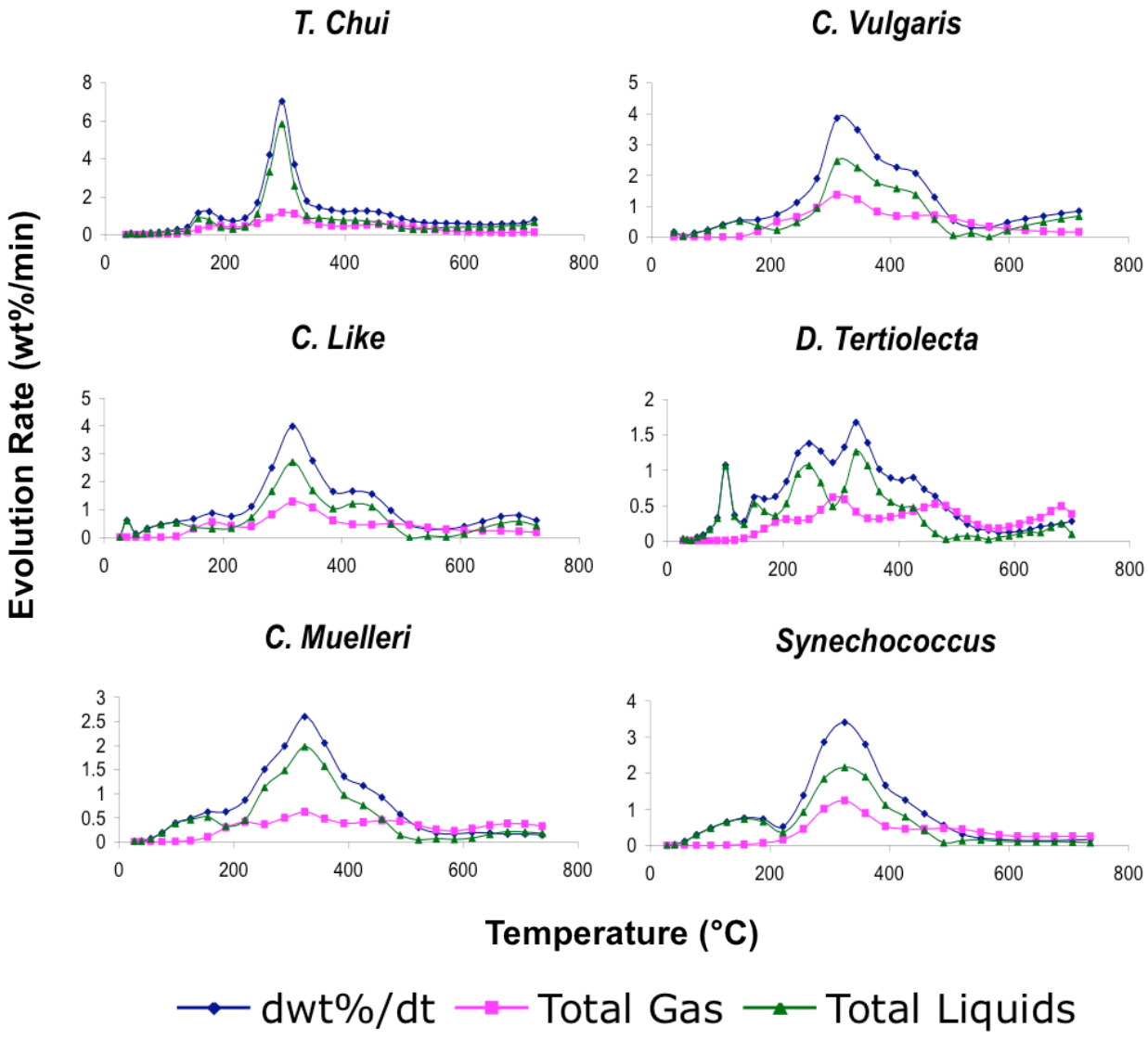


Figure 10. Rate of weight loss from microalgae from slow pyrolysis of microalgae superimposed to the apparent specific heat for the heating rate of 10°C/min

Significant variation across species was also observed in relation to char production. The greatest amount of char was observed in *D. tertiolecta* (63%), with *C. muelleri* also yielding more than half its weight in this product (53%). *T. chui*, *C. vulgaris* and *C. like*

produced approximately one third of their weight in char under the same process conditions. *C. vulgaris* yielded the highest proportion of gas in relation to the other species.

Table 9. The percentage of char, gas and liquid products evolved from slow pyrolysis of microalgae at 500°C

Species	**Char (%)**	**Gas (%)**	**Liquid (%)**
T. chui	37	20	43
C. vulgaris	34	25	41
C. like	37	22	41
C. muelleri	53	14	33
D. tertiolecta	63	13	24
Synechoccocus	44	18	38

In addition to quantifying the extent to which pyrolysis liquids evolve with temperature, it is also of interest to understand any fundamental differences in the nature of this fraction across microalgae species. Examination of the molecular weight distribution of the oils using matrix-assisted laser desorption/ionization (MALDI) reveals significant variability in the tar profile between different microalgae species (Figure 11). *T. chui,* and to an extent, *Synechoccocus,* exhibited a clear tendency to produce lighter oils, whereas the other species presented a broader spread across the range from light to heavy oils. The profile of *Synechoccocus*, a cyanobacteria, revealed a defined peak at 339 amu that corresponds to a relatively high concentration of a single medium-weight oil as well as two other heavy oil fractions (522 and 550 amu) that register in large quantity. The average molecular weight calculated for the pyrolysis oils derived from each algae species further supports the superficial observation of difference in their profile (Table 10). This is calculated using the following expression:

$$MW = \frac{\sum (Intensity \times MW)}{\sum Intensity} \qquad \text{Equation (4)}$$

Further characterisation of these oils is useful in identifying their commercial value and any upgrading that may be necessary to counter acidity or to reduce oxygen content.

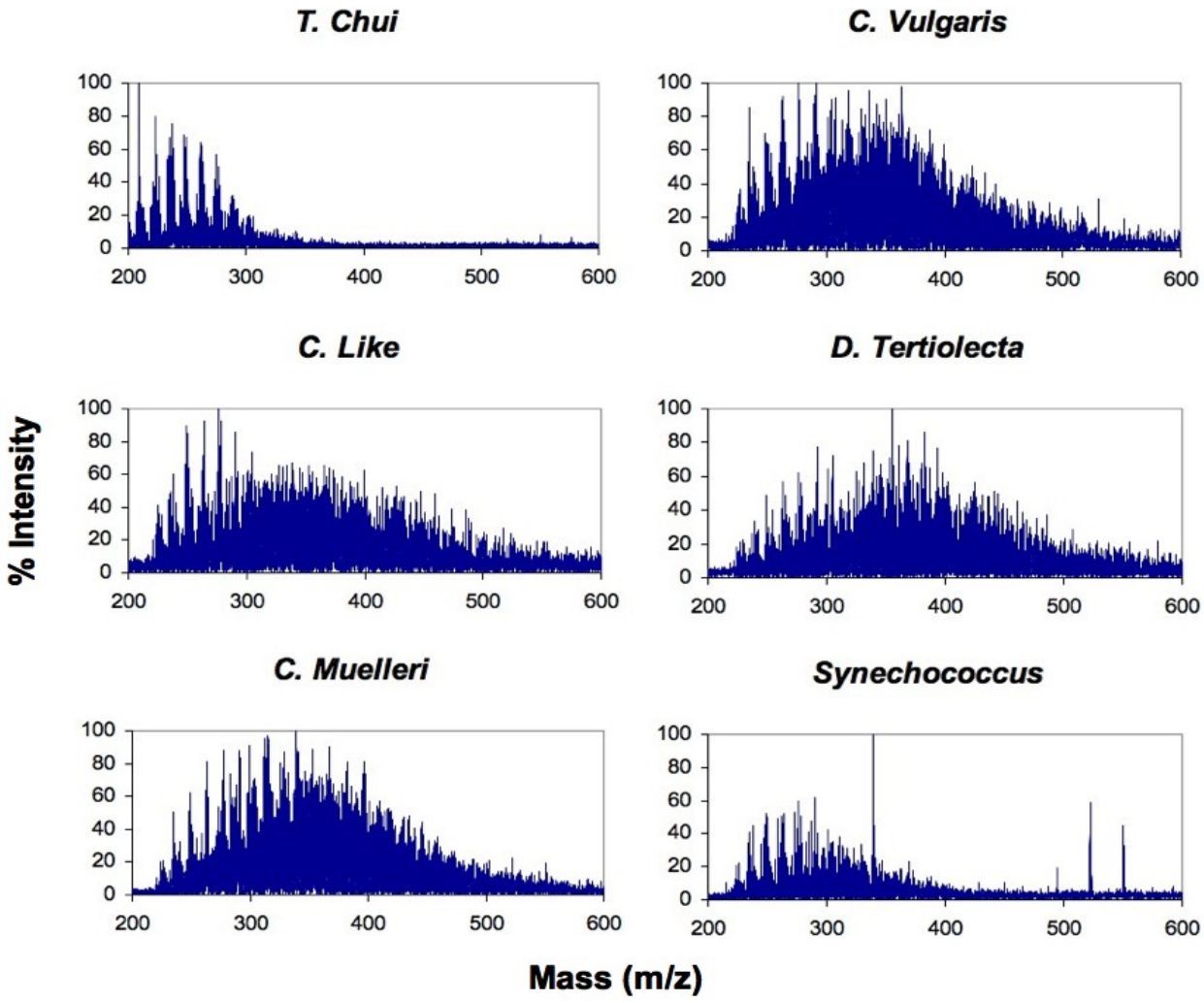


Figure 11. MALDI spectra displayed as molecular weight distribution of pyrolysis oils derived from microalgae

Table 10. Average molecular weight of pyrolysis oils derived by MALDI spectra

Species	Average molecular weight (amu)
T. chui	240
C. like	365
C. vulgaris	360
C. muelleri	370
D. tertiolecta	405
Synechoccocus	350

3.4 Conclusion

Aquatic microalgae have great potential for fossil fuel substitution in energy generation and conversion. When cultivated for this purpose, they have an advantage over energy crops by offering high growth rates that place no demand on arable land. Microalgae also offer promise for production of material feedstock substitutes, bio-chemicals and high volume carbon abatement. The work shown here investigates the thermal behaviour of a range of microalgae species when converted to biogas, bio-oils and charcoal under slow pyrolysis conditions.

The process energy requirements for pyrolysis of microalgae biomass to the temperature of 500^{o}C were found to be in a similar range (~ 1MJ/kg) for all of the selected microalgae species. However, the results indicate that there are fundamental differences in the thermo-chemical characteristics of the species studied in relation to a number of key indicators. Firstly, the ratio of evolved liquid, gas and char products to 500°C varied markedly across all species. Secondly, the rate and temperature of evolution of these fractions was also inconsistent. Thirdly, the mix of combustible volatile gas compounds that evolved with temperature was variable, resulting in differences in their combined calorific value. Finally, molecular weight distribution of the liquid fraction suggests that the composition and therefore likely value of pyrolysis oils differs between algae species.

Overall, the data suggest that the energy required to process microalgae biomass by slow pyrolysis to temperatures of 500°C is exceeded by the recoverable heating value of

combustible gases that evolve (under stoichiometric combustion conditions). This offers a processing route that could potentially be self-sustaining or ‘offset’ from an energy standpoint.

Chapter 4: Properties of oil and char derived from slow pyrolysis of *Tetraselmis chui*

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4.1 Introduction

Cultivating sustainable sources of high volume biomass for the production of fossil fuel substitutes is a key challenge to growth of the biofuel industry and the mainstream, marketable use of its derivatives. Greenhouse gas emissions and anthropogenic climate change concerns aside, competing demand for oilseed crops in global food, feed and fuel markets has added upward pressure to commodity prices and this threatens socio-economic stability, particularly in developing regions. This in turn places additional strain on the agricultural system and provides new inertia for intensive farming practices and land clearing for biomass cultivation that have led to questions about the sustainability of this approach (Rathmann et al., 2010).

Microalgae offer an attractive source of high volume biomass that does not compete for fertile, productive agricultural land or interact with established food or feed commodity markets. Many microalgae species can be beneficially grown in nutrient-rich waste or saline water streams and are known to be highly productive on a unit area basis when compared with terrestrial plants. Furthermore, given their positive response to artificial CO_2 supplementation, an opportunity for industrial ecology is emerging that sees microalgae cultivation co-located with emissions-intensive stationary power generators and heavy industry, such as coal-fired electricity plants (Maeda et al., 1995). In the short term this improves the emissions profile of stationary power generation, and may offset the consumption of fossil fuels depending on the processing route chosen and hence products derived.

Pyrolysis of microalgae at conventional commercial operating temperatures of <550°C potentially offers an attractive alternative option to direct extraction for derivation of valuable oil products. Thermal decomposition of biomass under controlled conditions gives rise to a pyrolytic oil with a distinctly different, highly complex and typically lower grade to that of natural vegetable or animal oils. Techniques for upgrading and refining pyrolysis oils for higher value applications, such as liquid transport fuels or chemical feedstocks, do exist, though the quality and extent to which this is possible varies both according to the species of biomass under consideration and the nature of the thermal decomposition process (Zhang et al., 2005; Strezov et al., 2007). In any case, a pyrolysis processing regime enables the focus to be placed on a highly productive biomass species (in this case, microalgae strains), where neither oil yield per hectare nor productivity need necessarily be compromised overall.

Limited examples of pyrolysis processing of microalgae biomass can be found in the literature (Wu et al., 1999a; Peng et al., 2001; Miao et al., 2004; Pan et al., 2010). However, the observation has been made that there is a direct relationship between the relative percentage of carbon and hydrogen found in biomass and therefore, the amount of hydrocarbons that can be obtained from it (Ginzburg, 1993). As such, microalgae may be a preferable source of biomass for hydrocarbon production via pyrolysis since they contain a high proportion of lipids, proteins and carbohydrates (Miao et al., 2004). This compares with the significant fraction of hemicellulose, cellulose and lignin found in woody biomass that typically contains a higher proportion of oxygen (approximately 40% by weight) that in turn yields a highly oxygenated and acidic pyrolytic oil that requires substantial upgrading and refinement prior to use (Mohan et al., 2006).

Fast or ‘flash’ pyrolysis that involves rapid heating rates to temperatures of >650°C and very short residence times (<1 second) is the preferred method to maximise the production of pyrolysis oil (Demirbas & Arin, 2002). Conventional slow pyrolysis technique, by contrast, employs slower heating rates typically around 5-20°C per minute. This translates to longer residence times and yields a much higher proportion of char (Bridgwater, 1999). Typical ratios of products from the slow pyrolysis of microalgae biomass are approximately one third of oil, gas and char, respectively, and this is

supported by the work presented in Chapter 3 (Grierson et al., 2009). From a commercial standpoint, slow pyrolysis is also run to a lower maximum temperature (<500°C) as this prevents secondary cracking and possible deterioration of the liquid fraction that is produced.

Biochar is similar to fossil coal that is produced through an analogous process of thermal decomposition of biomass (albeit over industrial processing rather than geological timescales). Evaluating the value of biochar in an agricultural context is now the subject of considerable research interest, as it has been shown to improve the productivity of soil and can enhance crop yields (Lehmann & Joseph, 2009; Hossain et al., 2011). Biochar offers numerous benefits when applied to soils and it potentially delivers a *net reduction* of atmospheric carbon dioxide, achieved across the combined cultivation and processing regime overall as a function of time (Lehmann et al., 2006; Ogawa et al., 2006; Lehmann & Joseph, 2009). Given that much of its volatile content has already been driven off with temperature, biochar is a highly stable, carbon-rich material, the half-life of which is measured in the hundreds, sometimes thousands of years. Critically, this substantially delays the release of CO_2 to the atmosphere that would otherwise be returned through biological decomposition, consumption and/or combustion of by-products or residues. Hence, an opportunity exists for establishing a value-adding biological carbon capture and storage (bio-CCS) solution through pyrolysis of biomass to produce char, that uses soil as the storage media.

The intent of this work is to further evaluate the pyrolysis behaviour of *T. chui*, a marine microalga, through characterisation of its pyrolytic oil and char fractions. The work then aims to explore the possible commercial applications, upgrading requirements and comparability of pyrolysis oils derived. As a potential soil amendment product derived from a saltwater species of microalgae, this paper also considers the implications for applying *T. chui* biochar in an agronomic context.

4.2 Experimental

4.2.1 Materials

Microalgae samples of *Tetraselmis chui* were selected as a reference species in this work. *T. Chui* strains have been shown to produce 17% of dry weight in lipid and are traditionally used for culturing of fish and oysters in the aquaculture industry due to their high nutritional value (Brown, 1991). In this work, *T. chui* biomass was initially cultured indoors under controlled conditions at the NSW Department of Primary Industries (Fisheries) laboratory in Port Stephens, Australia, wherein temperature, CO_2 enriched air flow (air + 2% CO_2) and light were controlled. A standard 'f/2' nutrient load (Guillard & Ryther, 1962) containing N, P, K & minerals was introduced to each new volume during cultivation. Bacterial infection during the transfer to progressively higher volume growth vessels was minimised by autoclaving all fittings and volumes.

Once the culture was stable in 20L carbuoys the solution was transferred to a 25 m^2 outdoor photo-bioreactor. The cultivation environment for this experiment was intended to provide a more accurate simulation of an industrial, high volume application. Under these growth conditions, the microalgae culture was exposed to natural sunlight, weather and fluctuations in operating conditions, such as temperature.

As soon as the culture matured and reached a stationary phase of growth in the photo-bioreactor, a sample was mechanically harvested by suspended solid centrifuge. The resulting slurry was then transferred to a cream separator to reduce the biomass to a thick paste and then initially dried in a conventional oven for at least 24 hours at 50-55°C. All samples were finally ground and dried at 70°C for 3 hours in a vacuum oven.

Pyrolysis liquid was produced by heating a 2.4g *T. chui* sample in a fixed bed infrared pyrolysis oven at 10°C/min up to a maximum temperature of 500°C, with inert helium passed through the packed sample cylinder at 50ml/min and argon (5ml/min) used to insulate the heating element that enclosed the glass cylinder. The sample was held at the maximum temperature for 20 mins to ensure thorough liquid conversion to 500°C. Glass wool was packed on either side of the biomass sample, and also at the

downstream end of the tube (in relation to the direction of gas flow), to hold the sample in place and to trap oil as it condensed at room temperature. Once the heating process was complete, the retained pyrolysis liquid held by the glass wool was dissolved using dichloromethane (DCM), then immediately frozen for temporary storage to minimise devolatilisation.

Pyrolysis char was obtained by packing 174g of dry microalgae biomass into a reactor crucible for use with a Labec HTF 90/12 horizontal tube furnace with a fixed bed. In an inert nitrogen atmosphere with a sweep rate of 100ml/min, a heating rate of 10°C/min was steadily applied up to a maximum temperature of 500°C, then held for 20 min to achieve thorough thermal decomposition to this threshold. The char was then collected and likewise frozen for temporary storage in readiness for analytical work.

4.3 Methods

4.3.1 Proximate and ultimate analysis of biomass, bio-oil and pyrolysis char

A proximate analysis and/or gross calorific value (CV) for both the unprocessed (raw) algae biomass, bio-oil and pyrolysis char were measured in accordance with Australian Standard Methods AS1038.3, AS1038.5 and AS4264.1. Ash composition of the char was also determined, according to AS 1038.14.3 and AS 4264.1. Ultimate analysis, initially determined on an air-dried basis, measured moisture (AS 1038.3), carbon/hydrogen (AS 1038.6.1), nitrogen (AS 1038.6.2) and total sulphur (AS 1038.6.3.3), where applicable.

Adjustments were then made for inherent moisture, hydrogen and sulphur correction (CV only) and conversion to a dry, ash free basis (dab) was undertaken for reporting purposes in this work. As per the Australian standard, proximate results are the mean of duplicate determinations that fall within prescribed tolerance ranges, rounded to the nearest 0.1%. CV is likewise reported as the mean of duplicate determinations to the nearest 0.01 MJ/kg, with a repeatability tolerance threshold of 0.13 MJ/kg. Carbon and hydrogen are also established as the mean of a duplicate run, with a reported range to the nearest 0.1% and 0.01% for each, respectively. Reported nitrogen and sulphur readings are the mean of two sample runs, each reported to within 0.01%.

4.3.2 Fourier Transform Infrared Spectroscopy (FT-IR) of pyrolysis liquid and solid samples

The FT-IR spectra of the pyrolysis liquid, in addition to the unprocessed microalgae and bio-char were recorded using a Nicolet 6700 FT-IR spectrometer applying an Attenuated Total Reflectance (ATR) method with a diamond crystal. The total number of scans was 32 with spectral resolution of $4cm^{-1}$. Omnic Spectra software was used to assist with interpretation of results, for which there was only a single scan undertaken.

4.3.3 Gas Chromatography - Mass Spectrometry (GC-MS) analysis of bio-oil samples

Analysis of pyrolytic oils was undertaken using a Shimadzu GC-MS apparatus (Model QP2010), with a 30 metre long SGE-BP1 column of 0.25µm diameter. Prior to commencement, the instrument was auto-tuned using perfluorotributylamine (PFTBA) as a calibrator.

The GC-MS method selected was a four-stage process, consisting of:

- Solvent purge of DCM at 45°C, held for 3 minutes
- Commencement of logging from 3 minutes
- Steady temperature increase from 45°C to 150°C at a heating rate of 5°C/min
- Steady temperature increase from 150°C to 300°C at a heating rate of 10°C/min and held at 300°C for 5 minutes

Using helium as a carrier gas, linear velocity was set at 35 cm/s with a split ratio of 20. Qualitative results were later synthesised and integrated using Shimadzu Lab Solutions GCMS solution software (Version 2.40). Reported results are limited to a single GC-MS analysis for each bio-oil sample.

4.3.4 Thermo-gravimetric analysis of liquid and solid samples

A Mettler Toledo thermogravimetric analysis (TGA) instrument (TGA/DSC 1 Stare System) operated with Stare software was variously employed to determine the weight loss of the samples with temperature. The raw, char and liquid samples were each placed in an aluminium cylindrical crucible with an additional empty crucible employed as a reference. TGA experiments were carried out using nitrogen as a carrier gas, flowing at

a rate of 20 ml/min, with a consistent heating rate of 10°C/min. In case of the bio-oil analysis, a method was applied to conduct proximate analysis using TGA. This method had an interim hold point at 110°C for 10 mins, to clearly delineate and enable all water to be evaporated and was held again at 900°C for 10 mins to ensure thorough removal of volatile matter, based on the method AS 1038.3-200, *Coal and coke - Analysis and testing, Part 3: Proximate Analysis of higher rank coal*[1]. Once this point in the process was reached, the temperature was raised to 1000°C and air introduced for 15 mins in order to burn off the remaining sample to establish ash content. Buoyancy correction was conducted using a blank experiment with no sample placed in the alumina crucibles prior to each sample run and each sample run was repeated in order to verify the nature of the thermal decomposition process.

4.3.5 Char characteristics and nutrient properties

Analytical work to determine the properties of the char was undertaken according to published standards. The methods employed were as follows:

- Soil pH ($CaCl_2$) – R&H 4B2 (Rayment & Higginson, 1992): involves detection of the change in potential in a glass-calomel electrode array or millivolt meter, standardised against buffer solutions of known pH.
- Available (Colwell) orthophosphate phosphorous – R&H 9B1 (Rayment & Higginson, 1992): employs an extracting solution of 0.5 M $NaHCO_3$ adjusted to pH 8.5 with NaOH, in a sample to solution ratio of 1:100, over 16 h at 25°C.
- Soil conductivity – R&H 3A1 (Rayment & Higginson, 1992): uses a conductivity cell and meter with a 1:5 soil/water suspension, based on used of air-dry soils.
- Organic Carbon – DPI in-house method 236 as per R&H 6A1, without particle size measurement (Rayment & Higginson, 1992): a wet oxidation method in which a blank is run, followed by testing with a reference material. H_2SO_4 is added to the sample wetted with a $Cr_2O_7^{2-}$ solution to achieve a chemical reaction.

[1] Since coal is essentially a form of ancient, fossilised biomass, and this technique aims to measure common (proximate) properties of interest (inherent moisture, fixed carbon, volatile matter and ash), this method is considered appropriate despite the differences in ratio of these in a microalgae biomass sample.

- Total carbon and total nitrogen by Dumas combustion method – DPI in-house method 630 as per ISO 10694, with inclusion of Total N also: 2 blanks are analysed in the beginning, and the sample was repeated with Glutamic Acid drift standards; reference material run also included for both TC and TN.
- Determination of Gillman and Sumpter exchangeable cations by ICP – R&H 15E1 (Rayment & Higginson, 1992) + USEPA 6010: involves treatment with (unbuffered) 0.1M $BaCL_{2,}$ typically used to measure highly weathered tropical soils.
- Mineral nitrogen KCl extraction – R&H 7C2 (Rayment & Higginson, 1992): uses a flow injection analysis (FIA) technique in which a peristaltic pump draws sample in and is mixed with the reagant, namely 2 M KCl in a 1:10 sample to solution ratio held for 1 h at 25°C.
- Trace elements in the char were detected by the National Measurement Institute according to the Australian standard (NT2_49): uses a combination of methods as required for detection of different elements, as per AS 1038.10.1-5. The standard requires minimum reporting levels for each trace element, below which the levels are considered of no interest.
- X-ray Diffraction (XRD): The mineralogical characterization of the char was demonstrated using a Phillips MPD XPert Pro: Cu Kα radiation, λ = 1.5406 Å, operating conditions of 45kV and 40 mA. XRD patterns were obtained on random powder specimens at 10−100° 2θ at a step size of 0.026°. For data analysis and interpretation PANAnalytical's 'Highscore Plus' software was used. Char samples were run in duplicate to ensure congruency of spectra.
- Mercury porosimetry was employed to determine the porosity and density of the pyrolysis char (DR 81321); This technique determines broad pore size distribution ranges and relates mercury intrusion pressures to pore size using the Washburn equation. The experimental work was carried out using a Micrometics AutoPore IV 9500 V1.06 machine.

4.4 Results and Discussion

Previous work presented in Chapter 3 revealed that a selection of microalgae species have a tendency to produce amounts of between 24 to 43/wt% pyrolytic oil, and 34 to 63/wt% char when pyrolysed to temperatures of 500°C (Grierson et al., 2009). In this work, FT-IR results comparing raw *T. chui* biomass with its subsequent pyrolysis liquid and biochar fractions (Figure 12) indicate that some of the detected group frequencies are common across multiple phases of the sample while others are unique and represent the signature by-products of thermal degradation.

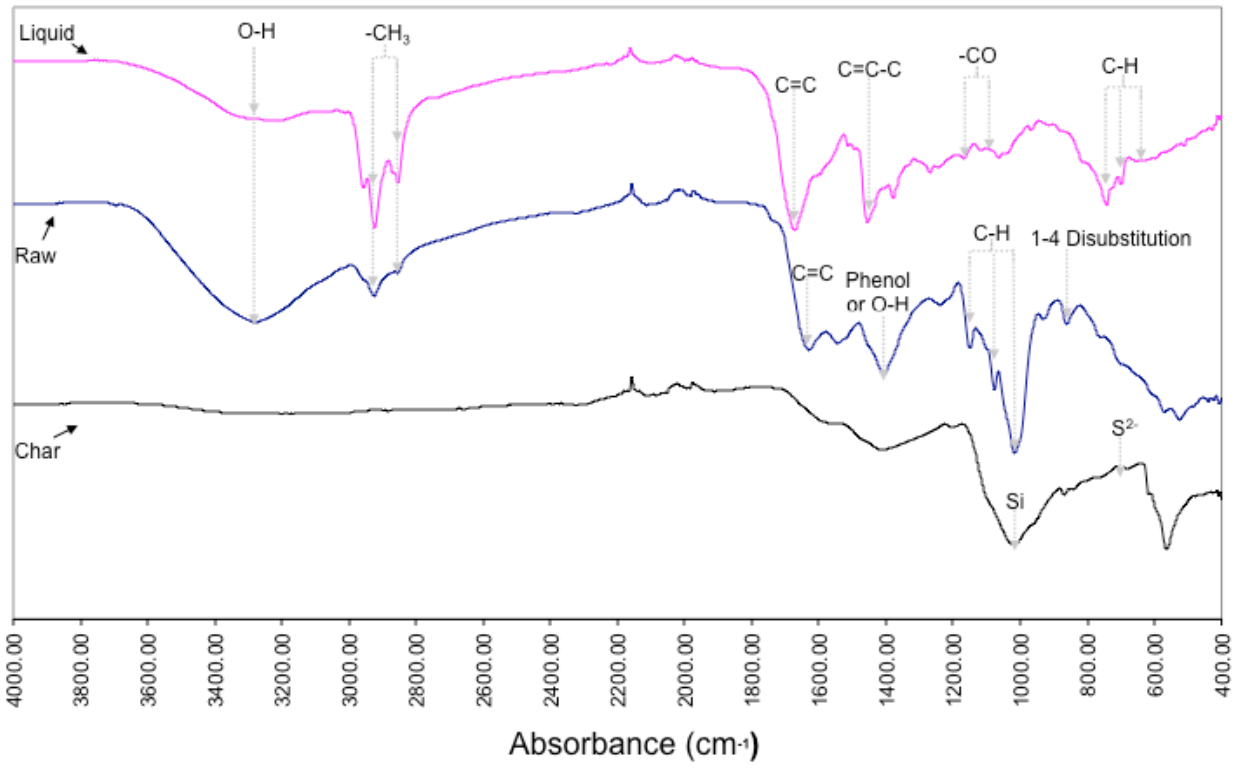


Figure 12. FT-IR spectra of solid samples and liquid derived from slow pyrolysis of *T. chui*

In both the raw and liquid samples, the presence of a distinctive O-H group at between 3400-3200 cm^{-1} is associated with water. Likewise, a methyl group ($-CH_3$) with asymmetrical/symmetrical stretch is evident in both the raw and liquid fraction between 2970-2950 cm^{-1} and 2880-2860 cm^{-1} and is a marker of saturated aliphatic hydrocarbons. At 1671 cm^{-1} in the liquid fraction a characteristic carbonyl group can be

identified, possibly an amide, reflecting the likely presence of degraded proteins. At a similar frequency, a C=C bond detected at 1628 cm^{-1} with moderate intensity in the raw sample suggests an aryl substituted (unsaturated) alkene.

Phenol (or a tertiary alcohol) is implied through FT-IR by a frequency reading of 1401-1310 cm^{-1} in the raw sample. A range of peaks in the liquid between 1100-1200 cm^{-1} are indicative of similar alcohol and hydroxyl groups, specifically a likely C-O stretching bond. Aromatic C-H groups with an in-plane bend can be observed in the raw algae and an aromatic C=C-C functional group with a ring stretch is detected in the liquid at 1454 cm^{-1}. The strong aromatic nature of the liquid is further corroborated by a series of compounds lying in the 900-670 cm^{-1} range, signalling the likely presence of additional aromatic out-of-plane bend C-H groups. A frequency in the 860-800 cm^{-1} range can be associated with a 1,4-Disubstitution (para) formation and is further evidence of aromatic compounds. Finally, in the biochar fraction, sulphides are detected at 710 cm^{-1}, with silicates also represented at 1013 cm^{-1}. Other peaks detected at low frequency in the biochar fraction below 600 cm^{-1} represent the presence of various inorganic compounds found in the ash.

Further analysis of the bio-oil using GC-MS presents a more detailed characterisation of the liquid fraction in this work, assisting with identification of discrete compounds. The major peaks detected by GC-MS have been isolated, numbered sequentially and presented according to retention time in Figure 13 and Table 11.

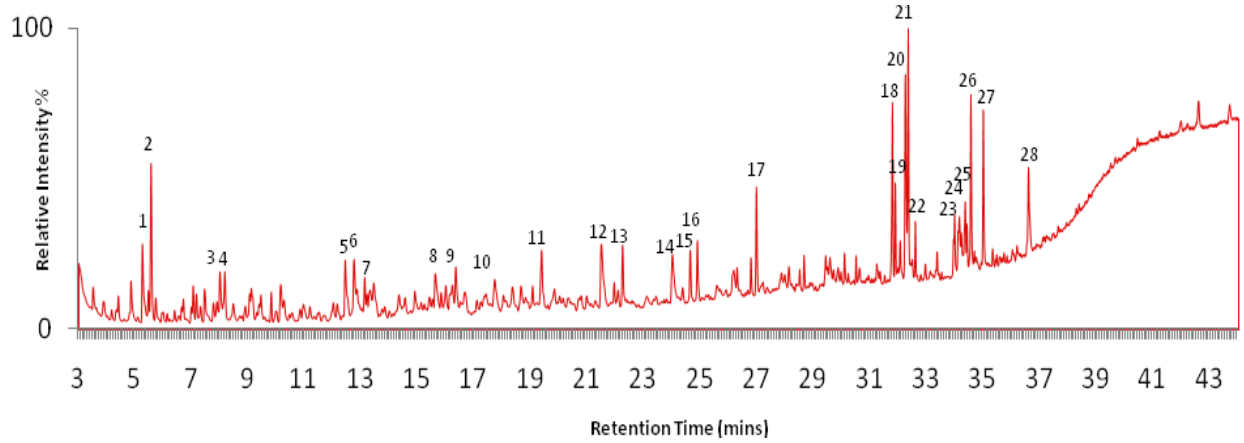


Figure 13. Pyrolysis oil species detected by GC-MS (*T. chui*)

The sample exhibits a range of fatty acids, alkanes, alkenes, amides, aldehydes, terpenes, pyrrolidinines, phytol and phenols. Prominent amongst these are nitrogen containing compounds, most likely due to the high protein content and chlorophylls found in the algae (Miao et al., 2004), correlating with FT-IR results.

According to GC-MS, aromatic hydrocarbons, including benzene and toluene, are detected and a significant number of compounds register in the C_{16}-C_{20} bracket, including methyl esters. *2-heptadecanone* is prominent, a common chemical building block utilised by industry for the production of fragrances and artificial flavourings. High molecular weight aliphatic amides are identified as *Hexadecanamide* or *Octadecenamide*, compounds regularly utilised in commercial applications as waterproofing agents, waxes, plastics and lubricants. Overall, the building blocks for liquid transport fuel and chemical production are present in the sample. With distillation and bio-oil upgrading using techniques such as catalytic hydrotreatment, many chemical species in the pyrolysis liquid produced from *T. chui* could be isolated and converted into commercial products (Zhang et al., 2005).

The calorific value (CV) of both the gas (2.9 MJ/kg) and char (14.5 MJ/kg) fractions of this strain of *T. chui* formed under slow pyrolysis conditions have been established experimentally, in addition to the CV of the raw algae sample (16.1 MJ/kg). Thermodynamic principles suggest that a CV for the liquid fraction can therefore also be derived from the following relationship where the density of the gas is 891.8 Kg/m^3 and Cp relates to the specific heat of reaction (as per Grierson et al 2009 and Chapter 3):

$$\boldsymbol{CV_{algae} = [\rho \text{ (density)} * \text{Integral of Cp to 500°C (J/kg)}] + [\text{mass fraction gas} * CV_{gas} \text{ (J/kg)}] + [\text{mass fraction char} * CV_{char}] + [\text{mass fraction oil} * CV_{oil}]} \quad \textit{Equation (5)}$$

Table 11. Pyrolysis oil species detected by GC-MS (*T. chui*)

Key	Ret. Time (mins)	Name	Area %	Formula
1	5.244	Pyrrole	1.88	C_4H_5N
2	5.548	Toluene	2.9	C_7H_8
3	7.982	Pyridine, 3-methyl-	1.18	C_6H_7N
4	8.158	2-Furanmethanol	1.14	$C_5H_6O_2$
5	12.411	2,4-Dimethyl-2-oxazoline-4-methanol	1.62	$C_6H_{11}NO_2$
6	12.724	Phenol	1.54	C_6H_6O
7	13.42	1,2-Cyclopentanedione, 3-methyl-	1.41	$C_6H_8O_2$
8	15.596	2-Undecanone, 6,10-dimethyl-	1.37	$C_{13}H_{26}O$
9	16.318	Undecane	1.18	$C_{11}H_{24}$
10	17.693	Phenol, 2,5-dimethyl-	1.04	$C_8H_{10}O$
11	19.351	Benzene, (2-methyloctyl)-	1.45	$C_{15}H_{24}$
12	21.464	Indolizine	2.33	C_8H_7N
13	22.214	Tridecane	1.09	$C_{13}H_{28}$
14	23.974	1H-Indole, 3-methyl-	1.57	C_9H_9N
15	24.604	3-Hexadecene, (Z)-	0.88	$C_{16}H_{32}$
16	24.857	Cyclododecane	1.11	$C_{12}H_{24}$
17	26.944	Heptadecane	1.77	$C_{17}H_{36}$
18	31.75	3,7,11,15-Tetramethyl-2-hexadecen-1-ol	2.7	$C_{20}H_{40}O$
19	31.852	3-Eicosyne	1.24	$C_{20}H_{38}$
20	32.207	Hexadecanenitrile	3.83	$C_{16}H_{31}N$
21	32.308	2-Heptadecanone	3.46	$C_{17}H_{34}O$
22	32.562	Hexadecanoic acid, methyl ester	0.77	$C_{17}H_{34}O_2$
23	34.115	Hexadecenenitrile	1.09	$C_{16}H_{29}N$
24	34.323	7-Octadecenoic acid, methyl ester	1.57	$C_{19}H_{36}O_2$
25	34.385	9-Octadecenoic acid (Z)-, methyl ester	0.64	$C_{19}H_{36}O_2$
26	34.524	Phytol	2.73	$C_{20}H_{40}O$
27	34.962	Hexadecanamide	2.4	$C_{16}H_{33}NO$
28	36.559	9-Octadecenamide, (Z)-	1.97	$C_{18}H_{35}NO$

Overall, this calculation indicates a total CV (expressed as HHV) for the liquid fraction of 22 MJ/kg, slightly higher than the 16-19 MJ/kg typically produced from wood (Mohan et al., 2006). However this liquid also includes water and analysis of the pyrolysis oil using TGA, shown in Figure 14, reveals that the water content of the liquid fraction is approximately 21.5%. By further derivation therefore, it can be calculated that the energy content of the oil component is approximately 28 MJ/kg (HHV). This compares with previous findings in relation to microalgae, namely that pyrolysis oils can be expected to contain a HHV of 29MJ/kg, depending on growth and processing parameters (Miao et al., 2004). Notably, in the Miao et. al. (2004) study, the energy content reported was the product of fast pyrolysis, with much shorter residence times and higher temperature.

Ultimate analysis results for the bio-oil are presented in Table 12. An alternative method for determining approximate HHV on the basis of these results is based on the ration of C, H and O. There are many different published formulae that adopt this approach, many of which were examined in a comprehensive review that settled on a proposed correlation, as follows, on which more than 90% of predictions fall in the range of <5% error (Sheng & Azevedo, 2005):

$$HHV\ (MJ/kg) = -1.3675 + 0.3137\,C + 0.7009\,H + 0.0318\,O \qquad \textit{Equation (6)}$$

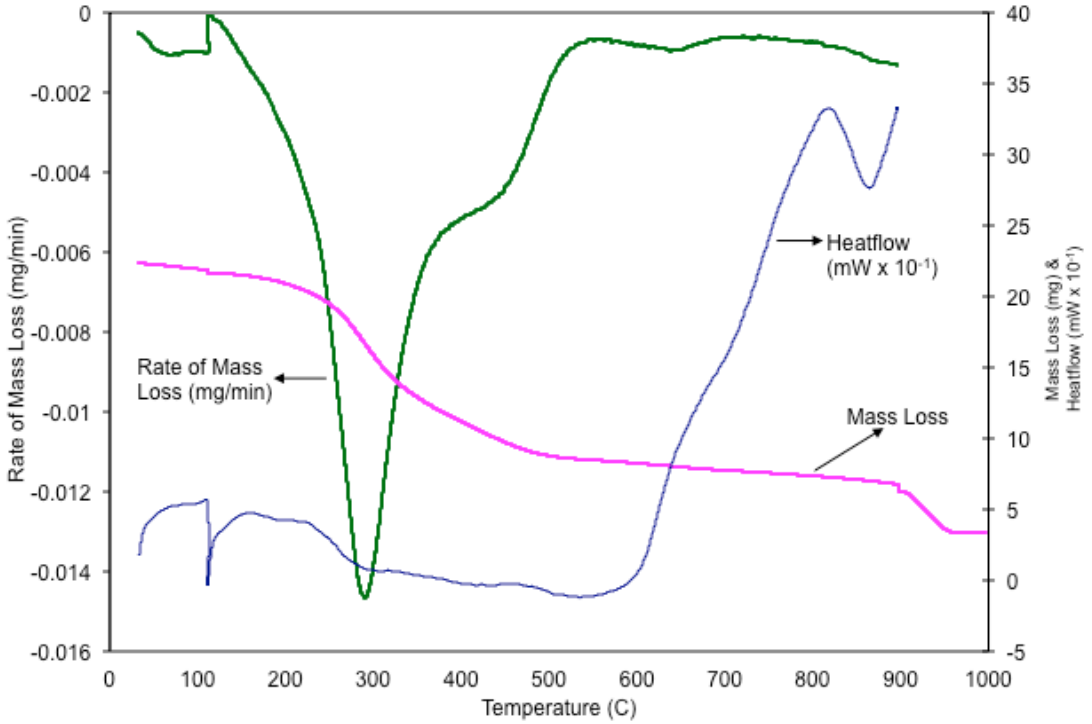
On this basis, an estimated HHV of 29.4 MJ/kg (+/- 5%) for the *T. chui* bio-oil based on ultimate analysis derivation is commensurate with the literature and in turn, the aforementioned derivation.

Table 12. Ultimate analysis of *T. chui* pyrolysis bio-oil

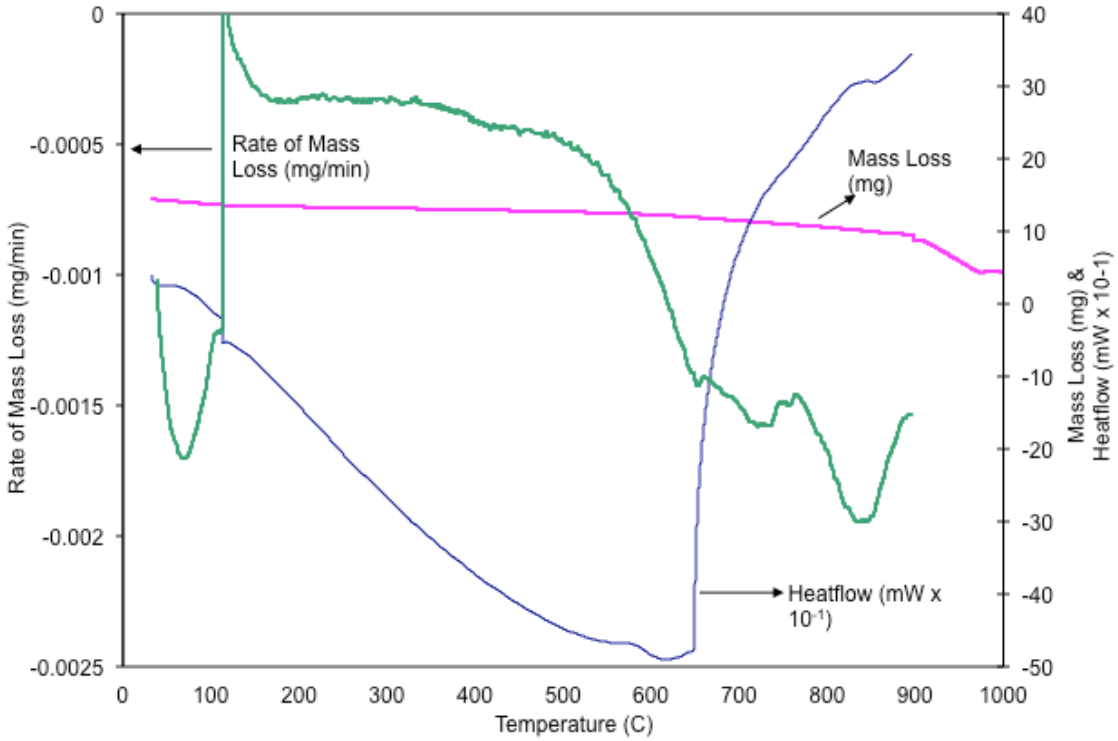
	Ultimate analysis (dry, ash free basis)				
	C%	**H%**	**N%**	**O%**	**S%***
Bio-oil	**76.3**	**9.5**	**8.3**	**5.2**	**0.8**

**S derived from Total Sulphur, hence Oxygen content is only an estimate*

(a)


Rate of Mass Loss (mg/min)
Mass Loss (mg) & Heatflow (mW x 10⁻¹)
Temperature (C)
Heatflow (mW x 10⁻¹)
Rate of Mass Loss (mg/min)
Mass Loss
0
-0.002
-0.004
-0.006
-0.008
-0.01
-0.012
-0.014
-0.016
40
35
30
25
20
15
10
5
0
-5
0
100
200
300
400
500
600
700
800
900
1000

(b)


Rate of Mass Loss (mg/min)
Mass Loss (mg) & Heatflow (mW x 10-1)
Temperature (C)
Rate of Mass Loss (mg/min)
Mass Loss (mg)
Heatflow (mW x 10⁻¹)
0
-0.0005
-0.001
-0.0015
-0.002
-0.0025
40
30
20
10
0
-10
-20
-30
-40
-50
0
100
200
300
400
500
600
700
800
900
1000

(c)

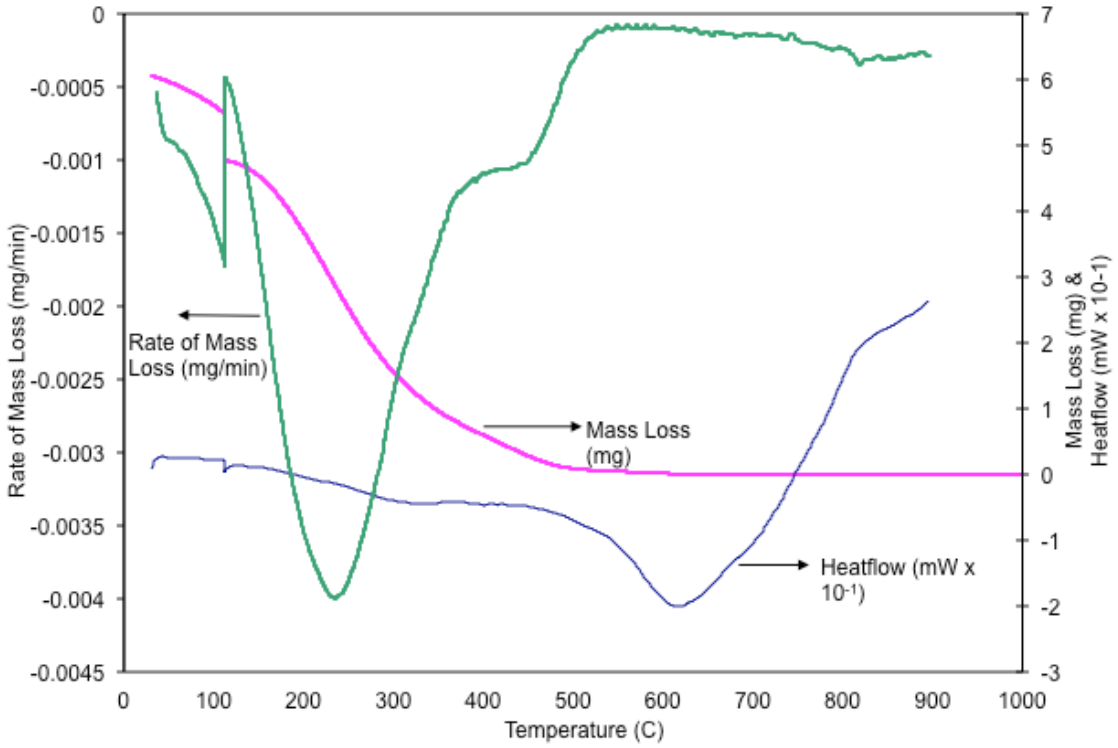


Figure 14. Thermogravimetric analysis of (a) raw, (b) char and (c) liquid samples (*T. chui*)

The CV, Proximate and Ultimate Analysis results of the raw and biochar samples are presented in Table 13. At 12.9%, the fixed carbon content of microalgae biomass is similar to wood, rapeseed and sunflowers (Strezov et al., 2003b; Sanchez et al., 2009), while volatile matter is lower. Elevated N levels were detected in the *T. chui* sample when compared with other forms of unprocessed biomass (Strezov et al., 2003b), attributable to the high protein content of microalgae. N is typically transformed into NH_3 during pyrolysis, which adsorbs to the biochar and is believed to act as a slow release mechanism (Clough et al., 2013). HCN is also known to result from the thermal degradation of biomass, produced from the cracking of cyclic amides formed as primary pyrolysis products (Hansson et al., 2004; Yuan et al., 2010). Nevertheless, it appears that the N fraction does not greatly concentrate in the char fraction as some of the N is lost through the evolution of amides and other compounds present in the tar (see Table 12). However N levels in the biochar are nevertheless still very high and are a similar level to that found in sewage sludge char (Bridle & Pritchard, 2004).

Table 13. Proximate and Ultimate Analysis of *T. chui* biomass and biochar

		Proximate (air dried basis)				**Ultimate (dry, ash free basis)**				
	CV (MJ/Kg)	**IM%**	**VM%**	**FC%**	**Ash%**	**C%**	**H%**	**N%**	**O%**	**S%**
Biomass	16.1	3.2	68.9	12.9	15.0	46.3	7.8	4.8	40.5	0.6
Biochar	14.5	6.2	32.6	30.9	30.3	57.8	2.8	5.5	33.6	0.3

CV = Calorific Value; IM = Inherent moisture; VM = Volatile matter; FC = Fixed carbon

The raw *T. chui* biomass has a moderately high ash content (15%/wt) that places it in the upper mid-range when compared with other biomass materials, such as coconut shell (0.7%), willow wood (1.1%), bagasse (2.9%), wheat straw (11.2%) and rice straw (23.5%) (Raveendran et al., 1995). In general, woody feedstocks consistently demonstrate a low ash content, whereas grass, straw and husk register a high percentage of ash mostly due to their elevated silica content. As a unicellular green algae found in marine environments, *T. chui* cells grow in a saline environment and so a high ash level is not unexpected.

Typically for pyrolysis processing, the inorganic mineral content present in the raw sample is enriched in the char during thermal decomposition. Overall, the very high ash value detected in the biochar product is similar to marine species of macroalgae (Bird et al., 2011). The ash is measured at 30%/wt using TGA (Figure 14), the composition of which is presented in Table 14. The high level of SiO_2 detected in the biochar ash (11.1%) is consistent with the earlier observation of high mineral content (where Si provides support in the cellular structure of the feedstock biomass). Ash composition analysis also highlights calcium (CaO) strontium (SrO) and magnesium (MgO) contents that represent 37%, 16% and 8.5% (dry basis, respectively) of the ash produced – combined, more than 60% of the total ash component. Notably, sulphur is detected in the ash in large quantity (7.1%), however its presence is minimal in the char on a dry, ash free basis (ultimate analysis) suggesting that the bulk of it is mineralised as SO_3. Aluminium (as Al_2O_3) exhibits a similar trend, albeit its presence in the ash is somewhat

lower (1.8%). A comprehensive analysis of additional micronutrients detected in the char follows in Table 15.

Table 14. Ash composition of *T. chui* char

Ash Composition			**(%db)**
Silicon	as	SiO_2	11.1
Aluminium	as	Al_2O_3	1.8
Iron	as	Fe_2O_3	2.2
Calcium	as	CaO	37
Magnesium	as	MgO	8.5
Sodium	as	Na_2O	4.9
Potassium	as	K_2O	2.1
Titanium	as	TiO_2	0.02
Manganese	as	Mn_3O_4	0.12
Phosphorous	as	P_2O_5	10.0
Sulphur	as	SO_3	7.1
Strontium	as	SrO	~16
Barium	as	BaO	<0.01
Zinc	as	ZnO	0.05
Vanadium	as	V_2O_5	<0.01

The application of biochar to soil is the subject of a growing body of literature. While this continues to emerge as a new branch of soil science, many of the data sets relating to various biochar properties are either incomplete or inconclusive. Likewise, the classification and analytical methods for biochar are mostly adapted directly from soil testing standards and are still the subject of some discussion (Lehmann & Joseph, 2009). Hence, previous work relating specifically to microalgae biochar properties and application has not been found though a recent study of macroalgae biochar offers a useful point of comparison (Bird et al., 2011).

There are various factors that influence the properties and consequent agronomic value of a biochar including the pyrolysis processing conditions, the fundamental composition

and homogeneity of the biomass feedstock, plant growth conditions and the soil relevant to its application. In any case, the use of biochar as a soil amendment product is central to the commercial viability and appeal of the microalgae pyrolysis value chain, hence its elemental profile is of interest.

Table 15. Trace elements in *T. chui* char (mg/kg)

Antimony	0.11	Hafnium	0.39	Samarium	0.04
Arsenic	<0.05	Holmium	<0.01	Scandium	0.16
Beryllium	<0.01	Iridium	<0.01	Selenium	<0.05
Bismuth	<0.01	Lanthanum	0.1	Silver	0.09
Boron	130	Lead	18	Sulphur	10100
Cadmium	0.05	Lithium	0.62	Tantalum	<0.01
Cerium	0.2	Lutetium	<0.01	Tellurium	<0.01
Cesium	<0.2	Mercury	<0.01	Terbium	<0.01
Chromium	1.6	Molybdenum	0.79	Thallium	<0.01
Cobalt	1.2	Neodymium	0.05	Thorium	0.03
Copper	37	Nickel	5.1	Thulium	<0.01
Dysprosium	0.02	Niobium	0.02	Tin	1.2
Erbium	0.02	Palladium	0.23	Tungsten	0.02
Europium	0.02	Platinum	<0.01	Uranium	1.8
Gadolinium	0.02	Rhodium	0.99	Ytterbium	0.02
Gallium	0.09	Rubidium	14	Yttrium	0.29
Germanium	<0.01	Ruthenium	0.81	Zirconium	8.7
Gold	<0.02				

A critical aspect of this analysis is to recognise that total detected nutrients are less important than their actual *availability* in terms of plant uptake. Furthermore, some properties of the biochar can have both direct and indirect value in a soil amendment context. In addition to direct uptake of available nutrients by plants once added to soil, the physical structure of biochar can assist for instance in the prevention of leaching and overall retention of nutrients and moisture, or provide a suitable habitat for the enhancement of microbial activity (Glaser et al., 2001).

Although the precise stability of C in biochar is not yet fully understood and depends on many factors (Lehmann et al., 2009), what is known is that the application of biochar substantially increases the residence time of C in soil. From an atmospheric stabilisation perspective this effect can be leveraged as a kind of 'carbon pump' to contribute to a net reduction of CO_2, when coupled with high volume pyrolysis processing technology (Lehmann, 2007). Biochar has several possible implications in a carbon trading system on this basis, namely that an increase in stabilised (inorganic) soil C through the application of biochar can theoretically be measured and thereby traded as a C abatement product.

A range of parameters has been tested in relation to the agronomic and carbon biosequestration properties of *T. chui* biochar (Table 16). The Total C reading of 40% (lower than in the Ultimate reading due to the dry, ash free basis of this analysis) has direct bearing on both the amount of organic C that is able to be introduced to the soil, as well as its potential value for carbon biosequestration under a carbon abatement or trading regime. Futhermore, the Total C level detected in the biochar in this work is in a similar range to that produced from rice hulls, bark, grasses, husks and sludges (Antal & Grønli, 2003; Joseph et al., 2009).

Organic C levels essentially provide a measure of what is potentially available to soil microbes for short-term decomposition, mineralisation and exchange. The organic C level in *T. chui* biochar (16%) is indicative of residual volatiles that have not yet evolved (or have reformed) during thermal decomposition, as well as carbonates and other potentially bioactive compounds that interact with the soil. This is likely to include tars that could have the potential to actually inhibit plant growth and microbial activity through the formation of toxic organic compounds, the potential for which can only be assessed through agronomy trials. This implies that just over half of the Total C detected in the biochar (24%) remains stabilised within the structure of the material for an indeterminate amount of time.

Table 16. Agronomic properties of *T. chui* biochar

EC (Ds/m)	39
pH (CaCl2)	12
Colwell Phosphorus (mg/kg)	320
Total Nitrogen (%)	4.6
Total Carbon (%)	40
Organic carbon (%)	16
KCl exctractable Nitrate (mg/kg)	6.3
KCl exctractable Ammonium (mg/kg)	0.62
Exchangeable cations	
• Aluminium [cmol(+)/kg]	<0.03
• Calcium [cmol(+)/kg]	6.4
• Potassium [cmol(+)/kg]	79
• Magnesium [cmol(+)/kg]	1.2
• Sodium [cmol(+)/kg]	110
CEC [cmol(+)/kg]	200

EC = Exchangeable cations; CEC = Cation exchange capacity

Focusing on the stable C fraction only (Lehmann et al., 2009), estimates for the persistence of this component of biochar range from several hundred to ten thousand years or more and it is understood to be significantly more stable in soil than other organic materials added under the same conditions. This represents approximately 9%/wt of the original biomass feedstock in this study, given that this species yields 37% char by weight overall under slow pyrolysis conditions (Grierson et al., 2009). This derivation for *T. chui* is based on the amount of char produced from the feedstock biomass (37%) and the Total C reading within the char (40%), of which 16% is bio-available as Organic C. This leaves 24% of the total carbon in the char that is non bio-available, which equates to 9% percentage of the original feedstock (where the balance of carbon in the raw sample is converted to bio-oil or volatile gases during pyrolysis).

The literature indicates that the pH of biochar is typically alkaline, however it can be anywhere in the range of pH 4-12 (Lehmann, 2007). For instance, the biochar from *T. chui* is very alkaline with a pH of 12. This may present value in application to acidic soils, offering a liming effect however also suggests that the extremity of this parameter may limit its use to equally extreme acid soil environments. Additional evidence of a likely liming effect is the predominance of CaO as the largest ash component (Table 14).

Further chemical analysis investigates the presence of critical plant growth nutrients in the biochar. The total N reading as a percentage of weight of the biochar is given as 4.6%, whereas the available nitrogen measured as mineral N (ammonium-N + nitrate-N) is much lower at only 0.69%. This is possibly because much of the N (and S) in particular is organically bound in the char itself (Chan & Xu, 2009). Notably, the C:N ratio in *T. chui* biochar is quite low (10:1) and this is generally a positive indicator for the mobilisation and exchange of inorganic N (Chan et al., 2007).

In comparison with the green wastes featured in the Chan et al. (2007) study, the algae biochar sample has a high level of both (Colwell) P and K (exchangeable cations). Calcium and magnesium cation levels are moderate at 6.4 cmol/kg and 1.2 cmol/kg, respectively. Overall cation exchange capacity (CEC) in the algae biochar is high (200 cmol/kg), which coupled with the high pH, suggests that this biochar should be able to strongly retain and make available its nutrients and help to stabilise pH as a bioactive soil additive (Lehmann, 2007). This is further supported by the base saturation (BS) calculation that provides an indication of nutrient status as derived from K, Ca, P and Na cation readings (Metson, 1956), though it should be noted that the high reading for CEC could be partly distorted by the presence of soluble salts that are a known drawback of the analytical method:

$$BS = (K + Ca + P + Na) \times (100/CEC) \qquad \textit{Equation (7)}$$

Based on exchangeable cation results (Table 16), a BS of 98.3 for *T. chui* biochar is regarded as highly saturated. Furthermore, this result translates to a measure of leaching

tendency also indicating that the biochar is weakly leached and likely to retain its nutrient over time (Metson, 1956).

Of particular note is the excessive reading for sodium cations (110 cmol/kg) that make up the largest share of the principal cations reported. A measure of the sodium proportion within the cation mix is expressed as exchangeable sodium percentage (ESP), the relationship of which is derived as follows:

$$\textbf{\textit{ESP = Exchangeable [(Na)/(Ca + Mg + K + Na)] x 100}} \qquad \textit{Equation (8)}$$

As a marine species of microalgae, *T. chui* grows or is cultivated in saltwater, hence the presence of sodium cations in the biochar is an important consideration for pyrolysis processing and later potential soil application or remediation. This feature was also discussed by Bird et al. (2011) in relation to marine macroalgae. An ESP of 56% suggests that *T. chui* biochar is extremely sodic and dominates in comparison with the other major exchangeable cations present i.e. aluminium, calcium, magnesium and potassium.

An electrical conductivity (EC) level of 39 Ds/m (equating to approximately 25g/kg of salt) also designates this material as extremely saline. As a measure of soil salinity, this level is well beyond the upper growth threshold of even the most salt tolerant plants. EC is only a proxy for total soluble salt levels because the influence of various salts on soil particles differs according to the relevant ionic conductivities. Nevertheless, an approximate value for the percentage of total soluble salts can be obtained by simply multiplying the electrical conductivity by 0.34, in this case giving a value of 13.3% (Piper, 1944).

As a soil additive therefore, it may be the case that the powerfully sodic and saline nature of this biochar would restrict its application to soil, if it could be used at all. While it may be that the addition of this biochar to a large volume of soil could have marginal impact relative to the benefits of its application (e.g. in the context of an entire paddock), it could

certainly contribute to a rise in the salinity of the soil substrate over time, potentially creating an osmotic pressure that may make it more difficult for plants to draw water. However, Bird et al. (2011) note that many commercial fertilizers in use today contain high levels of nutrients in salt form that do not appear to have long term negative impact, provided that the soil is well drained so it is conceivable that the negative effects of high Na levels in *T. chui* biochar could be overcome.

Previous studies have identified that a relationship between Na and P exists also to the extent that, at least in soil, saturation with monovalent Na cations can lead to increased desorption of P (Curtin et al., 1993). In the case of a soil additive such as biochar this could have the effect of making P more available to plants by encouraging its discharge (Curtin et al., 1993). Moreover K, much like Na, is found in an unusually high concentration in *T. chui* biochar also (79 cmol/kg), suggesting that slow release of this nutrient into soil substrate may occur, contributing positive nutrient benefit.

X-ray Diffraction (XRD) technique further reveals the crystalline structure and composition of minerals present in *T. chui* biochar, with sylvite (KCl), halite (NaCl) and calcite ($CaCO_3$) detected as major phases in the sample (Figure 15). The presence of such structures is important in understanding the chemical and physical properties of the biochar material. Both Sylvite and Halite are soluble salts that corroborate the sodicity and salinity findings, whereas Calcite is a stable form of carbonate common in sedimentary rocks. Minor phases present in the sample include quartz (SiO_2) and possibly strontium sulphate ($SrSO_4$), supported by the high levels of these elements in the ash.

A final review of the physical characteristics of the biochar, namely in relation to its porosity and density, is also important for soil remediation and application (Table 17). *T. chui* biochar has a Total Pore Area of 19 m^2/g and this measure of surface area (similar to that found in clay) has significant bearing on the health of soil, particularly in relation to nutrient transport, moisture retention and microbial habitat. One possible explanation for the almost ten-fold increase in CEC in micro- versus macroalgae biochar could be due to the higher surface area in the former (Bird et al., 2011).

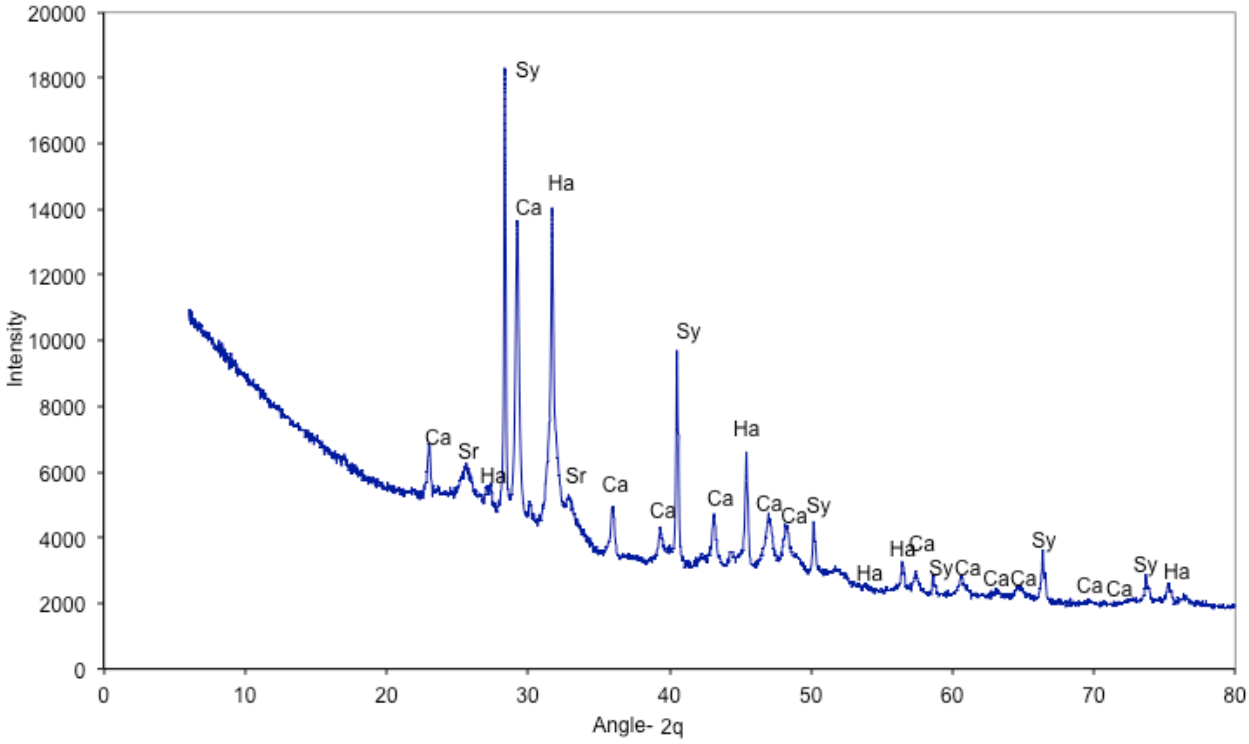


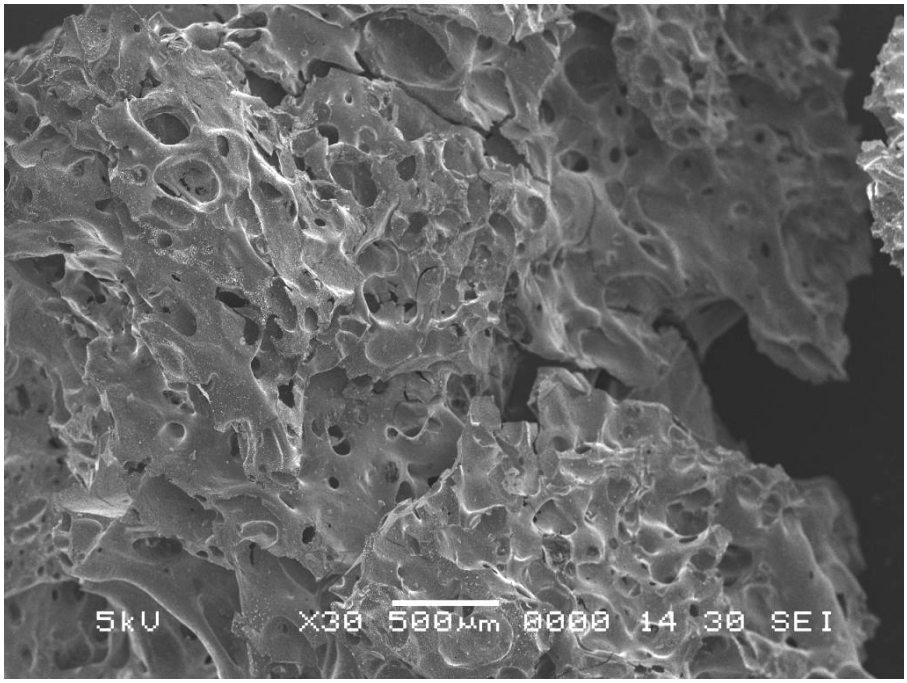
Figure 15. XRD patterns of *T. chui* biochar prepared at 500ºC.
(Legend: Ca=Calcite, Sy = Sylvite, Ha= Halite)

Table 17. Intrusion Data Summary - porosity and density of *T. chui* char

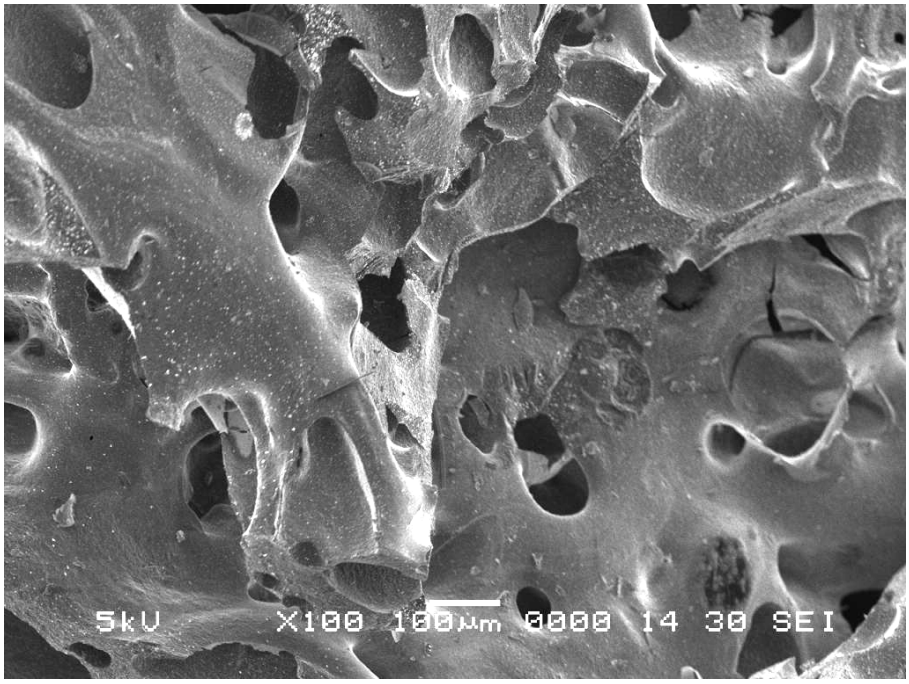
Total intrusion volume	1.0	mL/g
Total Pore Area	19.0	m^2/g
Median Pore Diameter (Volume)	55.9	µm
Median Pore Diameter (Area)	0.01	µm
Average Pore Diameter (4V/A)	0.2	µm
Bulk Density at 0.66 psia	0.8	g/mL
Apparent (skeletal) Density	3.3	g/mL
Porosity	76.3	%
Stem Volume Used	27	%

The average pore diameter reading of 0.2μm in the biochar, with a median diameter level of 0.01μm, indicates that the material has a wide variance of pore sizes, with a distribution of relatively few large macropores albeit an overwhelming majority of micropores present. Scanning electron microscope (SEM) images taken at magnifications of 30x, 100x and 500x confirm this observation (Figure 16). The material exhibits a high porosity reading of 76.3% (a measure of the open spaces between the solid structures of the material) and this is also reflected in the intrusion volume of 1.0 mL/g. Apparent (skeletal) density is 3.3 g/mL and the biochar has a relatively low bulk density reading of 0.8 g/mL.

(a) Biochar x 30



(b) Biochar x 100



(c) Biochar x 500

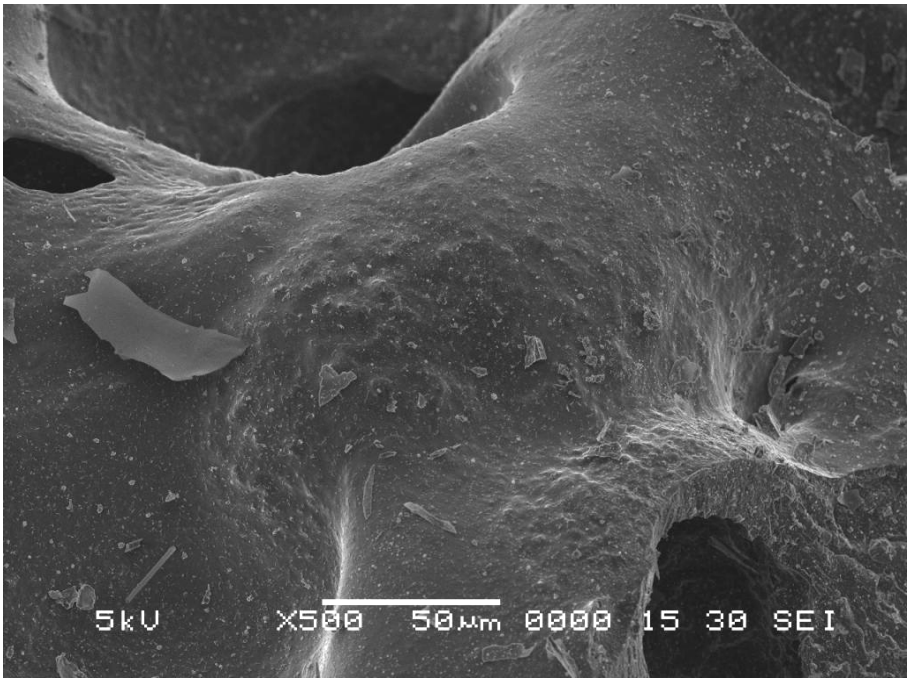


Figure 16. SEM images of *T. chui* biochar at (a) x30, (b) x100 and (c) x500

4.5 Conclusion

The liquid produced through slow pyrolysis of *T. chui* has a HHV of 27.9MJ/kg, exhibiting a large proportion of useful molecules in the C_{16}-C_{20} range. In the biochar fraction, the various properties detected indicate high potential for agronomic use, with appropriate caveats and subject to further study *in situ*. 9% of the carbon that resides in the char is in stabilised form, representing an enduring abatement opportunity when applied to soil. Overall, a diversified product portfolio realised through slow pyrolysis of microalgae may present a stronger commercial and environmental proposition than pursuit of a purely liquid fuel production regime alone.

Chapter 5: Assessment of bio-oil extraction from *Tetraselmis chui* microalgae comparing supercritical CO_2, solvent extraction and thermal processing

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5.1 Introduction

There are many technical and commercial challenges associated with the processing of biomass resources on an industrial-scale, requiring thorough investigation of the various trade-offs that come in to play (Wu et al., 2010). In the case of microalgae biomass, each link in the value chain offers scope for innovation and much work is currently being done to optimise critical steps such as cultivation, harvesting, dewatering, drying, transport and/or processing (Pienkos & Darzins, 2009). Once the microalgae has been cultivated it requires effective processing in order to derive maximum value. Since the natural lipid fraction in many species of microalgae has high potential for direct conversion to liquid transport fuel, efficient removal of the liquid fraction from the algal cells must be achieved in a manner that maximises production yields at acceptable cost (Mercer & Armenta, 2011).

Use of organic solvents for the extraction of oils from biomass is well known and this has been successfully trialled in the past for recovery of lipids from microalgae (Molina Grima et al., 2003). For instance, a variety of solvent techniques were trialled on *Botryococcus braunii* to extract fatty acid content, with up to 93.1% of total fatty acid content in the C_{16}-C_{18} range recovered (Tran et al., 2009). Likewise, ethanol was successfully used to extract 75% of the fatty acid content from the algae *Porphyridium cruentum* (Giménez Giménez et al., 1998). Many of the solvents commonly used for this purpose are eco-toxic, however they have the potential to be recovered and managed effectively to mitigate these risks. They also have the advantage of working with little additional process input, including energy, are relatively inexpensive and can be highly effective. Drawbacks include the fact that a large volume of solvent is often required to achieve

effective extraction and the solvent recovery process can be expensive both in terms of energy and cost (Mercer & Armenta, 2011).

Supercritical CO_2 (SC-CO_2) is an oil extraction technique also used in high-volume, commercial biomass applications (King, 2002). SC-CO_2 is commonly used in processes such as decaffeination or for isolating cooking oil from rapeseed and is acknowledged as a relatively benign means to achieve extraction of useful compounds from biomass, reducing or even eliminating the need for use of highly toxic organic solvents (Brunner, 2005). For food applications and thereby human consumption, SC-CO_2 is emerging as a preferred technique due to substantially reduced contamination risk, however in the context of liquid transport fuel substitutes this prospect is of less concern since it is not an ingested product.

SC-CO_2 has previously been trialed on both micro- and macroalgae and has demonstrated the general viability of this extraction technique for select species. Mendes *et al* found that in comparison with organic solvents such as hexane or acetone (extraction efficiency of 18.5% and 16.8%, respectively), SC-CO_2 provides a comparable yield of 13.3% by weight in lipid from a crushed sample of *Chlorella vulgaris* (Mendes et al., 1995). In a study of *Spirulina plantesis*, SC-CO_2 yielded 90% of extractable oils in only fifteen minutes at 700 bar and 55˚C, compared with almost six hours to achieve the same using Soxhlet extraction with hexane (Andrich et al., 2006). Likewise, SC-CO_2 is able to efficiently extract the poly-unsaturated fatty acid content from microalgae, providing selection sensitivity for additional compounds, such as chlorophyll that is otherwise insoluble at lower temperature and pressure (Balaban et al., 1996).

SC-CO_2 has several potential advantages over other oil extraction processes, such as solvent extraction or mechanical pressing, by providing higher selectivity of individual compounds, low toxicity and relatively fast processing times (Zougagh et al., 2004; Macías-Sánchez et al., 2007). Overall efficiency of extraction of fatty acid content appears to increase with both temperature and pressure, with optimum conditions for species such as *Bortyoccocus braunii, Dunaliella salina, Spirulina platensis* and *Chlorella*

vulgaris identified as lying between 40 – 55°C and 300 – 350 bar, depending on the desired length of chain for extraction (Herrero et al., 2006).

The use of SC-CO_2 with a co-solvent can also assist with improving the efficiency and/or profile of extracts, whilst substantially reducing the total volume of organic solvent required (Aresta et al., 2005). If a SC-CO_2 with co-solvent regime is adopted, temperature and pressure variations can have the effect of improving the selective removal of compounds in the oil matrix. Regardless of the polarity of the oil compounds that are sought or the co-solvent that is chosen accordingly, SC-CO_2 was reported to raise the efficiency of oil extraction by enhancing the ability of the solvent to diffuse through the sample (Raventos et al., 2002).

Another route to production of liquid biofuels from microalgae biomass is through thermal degradation via pyrolysis. Slow pyrolysis of microalgae to a typical commercial operating temperature threshold of 500°C offers an advantageous route to a broad spectrum of potentially useful commercial products, including biofuels and biochar (Grierson et al., 2009; Mulligan et al., 2009). The pyrolytic oil produced from microalgae has a distinctly different, typically lower-grade and more complex character than the natural lipid it produces under cultivation. However, a pyrolysis processing regime enables the overall focus to be placed on highly productive microalgae species where biomass yield per hectare and therefore carbon cycling is prioritised (Demirbas, 2006), as opposed to natural oil yield alone.

The purpose of this work is to investigate direct extraction of the natural fraction of lipid in a fast-growing, highly productive microalgae species (*Tetraselmis chui*) using organic solvents, SC-CO_2 and oil production through pyrolysis. *T. Chui* strains have been shown to produce 17% of dry weight in lipid and are traditionally used for culturing of fish and oysters in the aquaculture industry due to their high nutritional value (Brown, 1991). Additionally, natural lipid extraction combined with pyrolysis of the biomass residue is also investigated here as it potentially presents a two-step process in which a concentrated, high value lipid might be directly extracted in the first instance, leaving a

biomass residue from which a lower grade, higher volume pyrolysis oil fraction, in addition to biogas and biochar, could be derived.

5.2 Experimental

Microalgae samples of *Tetraselmis chui* were selected as a reference species in this work. *T. chui* biomass was initially cultured indoors under controlled conditions at the NSW Department of Primary Industry (Fisheries) laboratory in Port Stephens, Australia, wherein temperature, CO_2 enriched air flow (air + 2% CO_2) and light were controlled. A standard 'f/2' nutrient load containing N, P, K & minerals was introduced to each new volume during cultivation (Guillard & Ryther, 1962). Bacterial infection during the transfer to progressively higher volume growth vessels was minimised by autoclaving all fittings and volumes. Table 18 summarises the chemical and physical properties of the strain of *Tetraselmis chui* investigated in this work.

Table 18. Known physical and chemical properties of *Tetraselmis chui*

	Proximate Analysis (air dried basis)				**Ultimate Analysis (dry, ash free basis)**				
CV (MJ/Kg)	**IM%**	**VM%**	**FC%**	**Ash%**	**C%**	**H%**	**N%**	**O%**	**S%**
16.1	3.2	68.9	12.9	15.0	46.3	7.8	4.8	40.5	0.6

CV = Calorific Value; IM = Inherent moisture; VM = Volatile matter; FC = Fixed carbon

Once the culture was stable in 20L carboys the solution was transferred to a 25 m^2 outdoor photo-bioreactor. Under these growth conditions, the microalgae culture was exposed to natural sunlight, weather and fluctuations in operating conditions, such as temperature.

As soon as the culture matured and reached a stationary phase of growth in the photo-bioreactor, a sample was mechanically harvested by suspended solid centrifuge. The resulting slurry was then transferred to a cream separator to reduce the biomass to a

thick paste and then initially dried in a conventional oven for at least 24 hours at 50-55°C. All samples were finally ground and dried at 70°C for 3 hours in a vacuum oven.

A Dionex Accelerated Solvent Extractor (ASE) 300 apparatus was used to extract lipid from a finely ground and dried *T. chui* sample, using a solvent mixture of dichloromethane (DCM) and methanol (MeOH) in a 9:1 ratio (Richter et al., 1996). The sample of microalgae was spaced within a stainless steel extraction vessel using a quantity of inert baked sand. The extraction method incorporated 3 rolling cycles that involved a 5 minute preheating stage, a 5 minute heating stage and a 5 minute static stage, prior to a 70%/volume solvent flush over a 5 minute purge period. The operating parameters were 100°C at 103.4 bar (1500psi) pressure, with 3 x 300 second purge cycles applied.

This technique was repeated as long as an extract of material quantity could be detected, with the combined biomass and sand remixed between each run to ensure even distribution and maximum penetration of solvent within the vessel. The lipid from each run was accumulated in a glass bulb and the excess solvent reduced by rotary evaporation. The total lipid extract was quantified gravimetrically.

Three different supercritical CO_2 (SC-CO_2) extraction regimes were trialled in this study. In each instance, a 50ml stainless steel extraction column loaded with approximately 5g of ground, dry *T. chui* was connected to the system shown in Figures 17 and 18. Any remaining volume in the column was filled with glass spacing beads to distribute and pack the sample tightly and to prevent gravity from clogging the inlet pipe with algae prior to pressurisation. The CO_2 pump (ISCO Model 260D Syringe pump) was cooled to 4℃ and the pressurised CO_2 delivered to the extraction vessel through a heating coil. The extraction column and heating coil were immersed in a water tank, the temperature of which was controlled by a circulating heater (Thermoline). The outlet of the extraction column was connected to a ball valve that was placed upstream of a micro-metering needle valve. The extraction experiments were commenced when the system reached the pre-determined pressure and temperature.

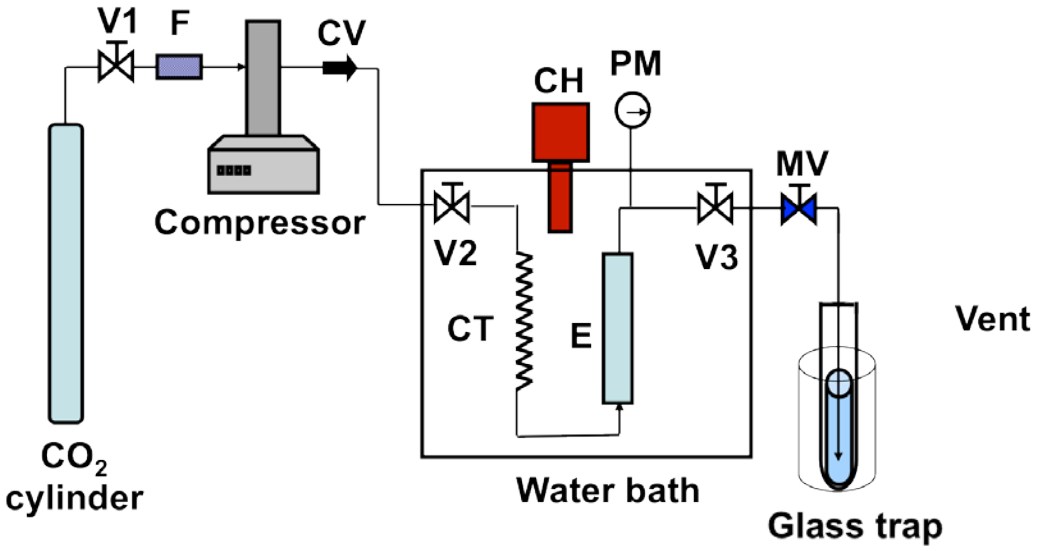

Figure 17. Schematic diagram of SC-CO_2 extraction.

(Legend: V1, V2, V3: stopping valve; F: filter; CV: check valve; HC: heating coil; E: extraction vessel; CH: circulating heater; PM: pressure meter; MV: micro-metering valve.)

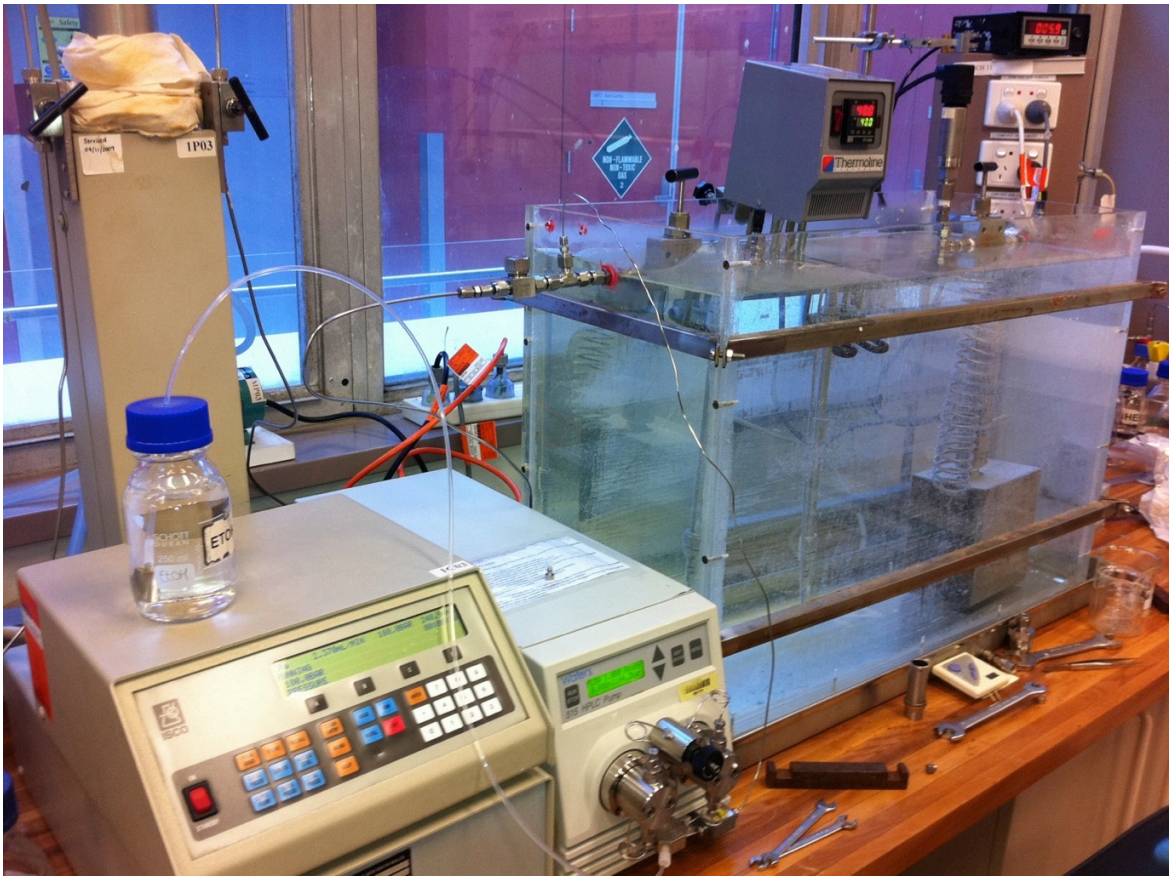

Figure 18. Photograph of SC-CO_2 extraction apparatus (UNSW)

There were two stages of extraction: static and dynamic. The static stages were approximately 30 min for all experiments, during which time the system was effectively sealed and held at constant pressure and temperature to allow full saturation with SC-CO_2. The subsequent dynamic stages varied from 30 to 50 min and maintained temperature and pressure, whilst allowing the extract to be pushed through the line into a collection tube. Alternation between static and dynamic stages only occurred when the volume of SC-CO_2 in the system required replenishment. The flow rate of CO_2 was kept at 2ml/min measured at operating pressure and 4℃ for all experiments.

As SC-CO_2 was expanded across the micro-metering valve during the dynamic stage, the extracted lipid was collected in a glass tube that was refrigerated between −20 and −5 ◦C in a cooling bath. After the experiments, residual extract that remained in the lines and valves was collected by flushing the line with the relevant solvent (methanol in the case of the 'neat' SC-CO_2 run). The solvent flush was thus ultimately mixed with the extract collected in the glass tube. This mixture was later placed in a rotary evaporator to remove the solvent, so the extracts could then be accurately weighed.

The first run involved 'neat' SC-CO_2 only, pressurised at 250 bar and held at 60℃. These relatively extreme SC-CO_2 parameters were selected for this regime since prior work with microalgae had suggested that extraction efficiency increases with both temperature and pressure (Mendes et al., 2003; Aresta et al., 2005; Herrero et al., 2006; Mendes et al., 2006). The second and third regimes involved use of supercritical CO_2 with the addition of methanol and then ethanol as co-solvents, respectively, at 180 bar and 40℃. These lower parameters were adopted as it was assumed that the addition of co-solvent would improve extraction efficiency without the need for such relatively extreme conditions.

Pyrolysis oils were obtained by separately heating 100mg samples of both raw microalgae biomass and post-extraction residues in an infrared pyrolysis furnace. The method incorporated a steady heating rate of 10°C/min, rising from room temperature to a maximum of 500°C (the typical threshold for industrial slow pyrolysis) and controlled by

a thermocouple attached to the wall of the furnace cylinder. Oils were condensed at room temperature and dissolved using dichloromethane (DCM), then immediately collected and frozen for temporary storage to minimise degradation. Further details of the experimental technique are discussed elsewhere in the literature (Strezov et al., 2003a; Grierson et al., 2009).

Aliquots were derivatised for GC-MS analysis with *N,O-bis(trimethylsilyl)-trifluoroacetamide* with *1*% *trimethylchlorosilane* (100 µL at 80ºC for 1 hour). Samples were separated on a DB5-MS column using an Agilent 7890A coupled to a Pegasus 4D time-of-flight mass spectrometer operating under the following program: isothermal heating at 40º for two minutes, then ramped at 4ºC/min to 310ºC, isothermal at 310ºC for 90 minutes. Compounds were identified on the basis of library mass spectral data, comparison with known standards, and from comparison with reported spectra from the literature. This technique is designed to convert fatty acids to fatty acid methyl ester (FAME), since highly polar compounds typically form hydrogen bonds that can clog the GC column and avoid detection. Derivatisation also helps to distinguish the unsaturated fatty acid component by neutralising the carboxyl functional groups through an esterification reaction.

Volatiles evolved during pyrolysis of microalgae and the post-solvent extraction residue were analysed separately by gas chromatograph. A M200 Micro gas chromatograph from MTI Analytical Instruments was connected to the gas outlet of the glass sample tube. A metallic molecular sieve 5A column (10m in length, 0.32mm diameter) at 90°C was used to separate H_2 and CO while analysis of CO_2, CH_4, C_2H_4, and C_2H_6 was performed on a bonded polymer Poraplot U column (8m in length, 0.32mm diameter) at 55°C. Chromatograms were obtained every 90 seconds using a gas thermal conductivity detector. Carrier helium gas at a rate of 50 ml/min was passed through 50 mg of biomass while maintaining a continuous heating rate of 10°C/min up to a maximum temperature of 750°C, to monitor compositional changes up to and beyond the industrial operating threshold of 500°C.

The Fourier Transform-Infrared Spectroscopy (FT-IR) spectra of the raw microalgae and the post-solvent extraction residues were recorded using a Nicolet 6700 FT-IR spectrometer applying an Attenuated Total Reflectance (ATR) method with a diamond crystal. The total number of scans was 32 with spectral resolution of 4 cm^{-1}. Omnic Spectra software was used to assist with interpretation of some of the spectra.

A Mettler Toledo thermogravimetric analysis (TGA) instrument (TGA/DSC 1 Stare System) operated with Stare software was employed to determine the weight loss of the unprocessed micro-algae and post SC-CO2 residue with temperature. The samples (weighing approximately 30 mg) were placed in a circular aluminium crucible with an additional empty crucible employed as a reference. All experiments were carried out using nitrogen as a carrier gas set at a flow rate of 20 ml/min, with a heating rate of 10°C/min up to a maximum temperature of 1000°C. The buoyancy correction for TGA data was conducted using a blank experiment with no sample placed in either of the crucibles prior to each sample run, with the sample run for both raw biomass and biomass residues performed in duplicate in order to confirm the pattern of thermal degradation behaviour.

5.3 Results and Discussion

The total lipids extracted from the strain of *T. chui* used in this work under the accelerated solvent extractor (ASE) conditions were 14.6 wt/%. This compares with the amount of 17% lipid recorded in the literature for the same species (Brown, 1991), variation of which may be accounted for by the differing cultivation conditions and genetic expression of individual strains, in addition to the efficiency of the solvent extraction method employed. Fractionation determined that the breakdown of oil fractions amounted to ~0.5wt% in aliphatic hydrocarbons, ~0.2wt% of aromatic compounds, with the majority of the balance (99.3wt%) being polar in nature.

Derivatisation of the extracts was essential as the polar fraction, specifically O-H groups, do not elute with the column used here and would not otherwise be observed by the mass spectrometer. Notably, H_2O is also a polar molecule, therefore the ASE

DCM/MeOH solvent mixture is likely to have removed residual moisture from the biomass in addition to lipids. Any moisture was later removed from the solvent mixture through the roto-evaporator and hence is not present in the derivatised, predominantly polar lipid sample.

The SC-CO_2 work with and without co-solvents, was undertaken with varying degrees of success in relation to oil extraction rates, which are compared to the ASE method in Table 19. SC-CO_2 extraction at 250 bar pressure and temperature of 60℃ managed to extract only the smallest detectable amount of lipid (0.01 wt%). This is most likely due to the highly polar nature of the natural oil found in *T. chui*. SC-CO_2 is well known to be most effective with extraction and selectivity of non-polar molecules and the aliphatic fraction in this case represents only around 0.05wt% (Hyatt, 1984). Subsequent SC-CO_2 runs utilising methanol (4.3 wt%) and later, ethanol (3.8 wt%) as co-solvents improved the bio-oil extraction ratio compared to pure SC-CO_2, however these extraction rates were lower than the extraction efficiency of the ASE method.

Table 19. Comparison of lipid extraction efficiency from *T. chui* using organic solvent, supercritical CO_2, supercritical CO_2 + MeOH, supercritical CO_2 + EtOH (wt%)

Method	**Extract (wt%)**
Organic solvent (DCM: MeOH)	14.6
Supercritical CO_2 (60°C / 250 bar)	0.01
Supercritical CO_2 + MeOH (40°C / 180 bar)	4.3
Supercritical CO_2 + EtOH (40°C / 180 bar)	3.8

This study reveals that SC-CO_2 method does not appear well suited to oil extraction from *T. chui* utilising the conditions studied in this work. Variations in temperature and pressure, in addition to the prospect of pre-treatment, such as cellular disruption of the microalgae, may improve SC-CO_2 extraction efficiency however this is only likely to be of value where a co-solvent is utilised, given the polarity of the lipids in this species. Considering the polar nature of water, it is also possible that an increase in the moisture

content of the sample could aid SC-CO_2 extraction of commensurately polar oil molecules to achieve the desired outcome.

Of particular note in this study was characterisation of the extracts derived in each of the four experimental regimes. The compounds detected by GC-MS in the pure SC-CO_2 solute were close to identical to those extracted by the solvent and SC-CO_2/co-solvent methods, despite differences in extraction volume overall (Figure 19). The most common compounds detected include a selection of free fatty acids (FFAs) extracted in varying concentrations, including both the mono- and poly-unsaturated form of *eicosanoic acid* (peaks VII and VIII). This substance is common to peanut oil and other fatty substances such as butter. Peak V in all samples corresponds to *Phytol*, with a chemical structure of $C_{20}H_{40}O$. *Phytol* is an ester-linked side-chain of chlorophyll-*a* and a biogeochemical marker in petroleum sediments (Didyk et al., 1978). As a material feedstock in the pharmaceutical industry, it is used to synthesise vitamin E and K_1 and potentially has direct commercial applications (Borowitzka, 1988). Peaks II, III and IV are related to *hexadecanoic acid* ($C_{16}H_{32}O_2$), otherwise known as *palmitic acid*. All fatty acids detected can have direct commercial application in the production of a petro-diesel liquid transport fuel substitute through the process of transesterification that forms biodiesel.

A major difference between the extracts is that pure SC-CO_2 was unable to remove some of the lightweight oil molecules from the microalgae biomass (not presented in Figure 19 as they elute substantially earlier), namely *glycerol*, *methyl 1H-indole* and *pyrimidine*, that are otherwise extracted in all cases where organic solvent is present. The solvent method is also able to extract *phytol*. A *phytol* peak is detected in the pure SC-CO_2 regime also, however not in the SC-CO_2 co-solvent runs. In each extraction regime, the major lipids (FFAs) are detected in similar ratios of abundance (Figure 20). As such, this suggests that there is no obvious selectivity of compounds taking place in relation to SC-CO_2 extraction compared to the organic solvent.

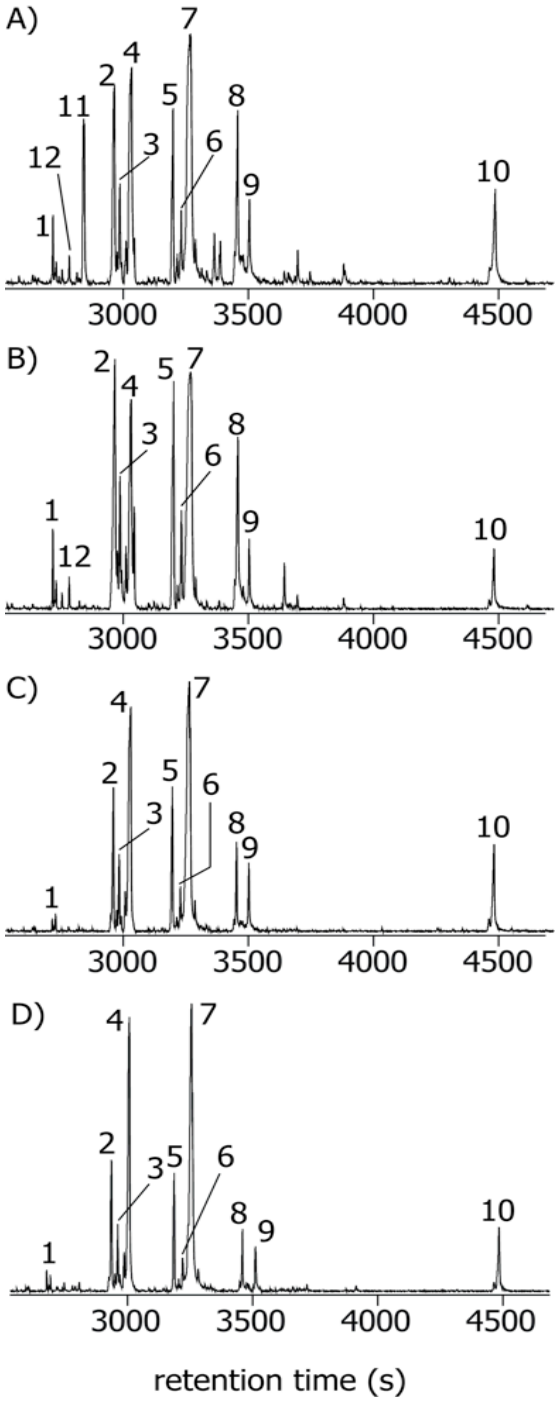

Figure 19. a) Total ion chromatogram (TIC) of natural lipid extract from raw *T. chui* using solvents (MeOH:DCM, 9:1); b) TIC of extract using pure SC-CO_2; c) TIC of extract using SC-CO_2 and MeOH co-solvent. d) TIC of extract using SC-CO_2 with EtOH co-solvent.

(Compounds detected (underivatised): 1 = tetradecanoic acid; 2 = polyunsaturated hexadecanoic acid; 3 = monounsaturated hexadecanoic acid; 4 = hexadecanoic acid; 5 = phytol; 6 = polyunsaturated octadecanoic acid; 7 = monounsaturated octadecanoic acid; 8 = polyunsaturated eicosanoic acid; 9 = monounsaturated eicosanoic acid; 10 = campesterol; 11 = siloxane; 12 = phytol.)

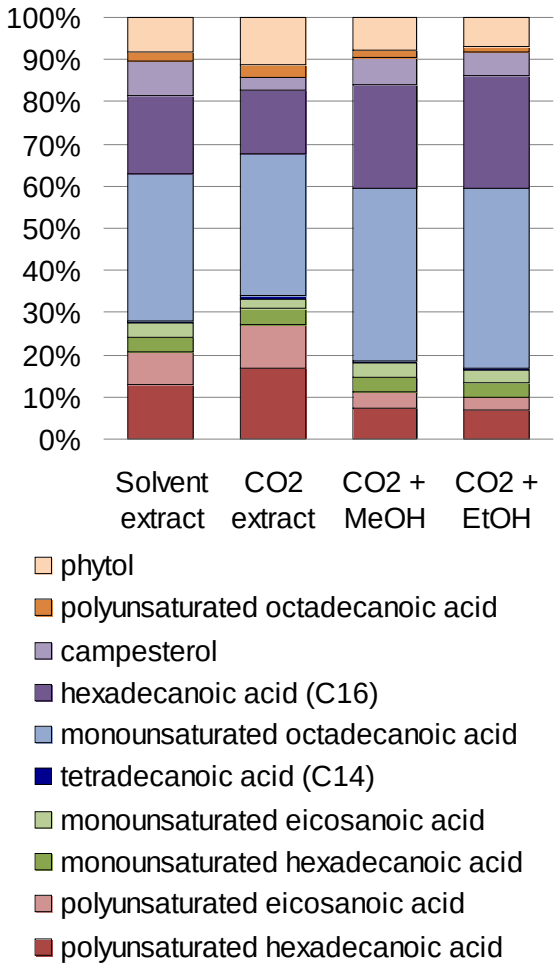

Figure 20. Comparison of extraction techniques and the oil species eluted, as a % of total extract weight (*T. chui*)

A sample of raw *T. chui* was compared with the post-solvent extracted residue derived from the same species, given the relative success of the organic solvent extraction approach in eluting most of the known natural lipid contained in this species. As shown in Figure 21, the FT-IR spectra of each of these two samples are similar and present bonds that are typically found in samples of biological origin. In particular, absorption bands detected in the FTIR spectra of the examined samples indicate the presence of lipids, proteins, peptides and sugars.

Protein absorption bands are associated with characteristic amide groups. A strong bond around 1628 cm^{-1} in both samples represents a C=O stretching coupled with C-N

stretching and also N-H bending vibrations. C-N and N-H also contribute to the bond detected around 1545 cm^{-1}, with further N-H bending exhibited as a weak peak around 760 cm^{-1}. Several of the bonds in the region between 1000 cm^{-1} and 1500 cm^{-1} are likely absorption markers for nucleic acids. For example, the bonds between 1250 cm^{-1} and 1500 cm^{-1} are due to vibration coupling between a base and a sugar, while in the range of 1000 cm^{-1} to 1250 cm^{-1} sugar-phosphate chains are observed.

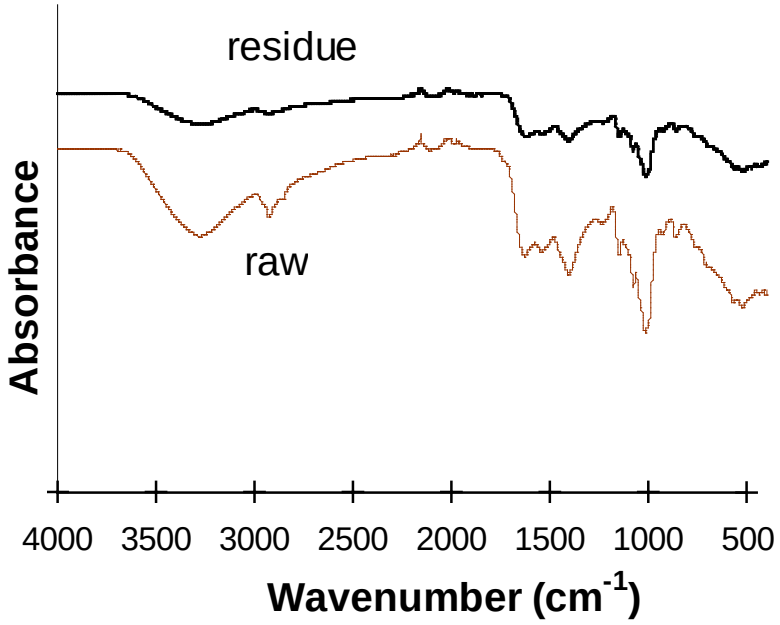

Figure 21. FT-IR results of raw algae (*T. chui*) superimposed over post-solvent extraction residue (*T. chui*).

Other bonds appearing in the region between 900 cm^{-1} and 1450 cm^{-1} are mostly due to molecular groups containing oxygen, carbon and hydrogen atoms. A peak at 930 cm^{-1} corresponds to C-O-H out-of-plane bending vibrations; at 1077 cm^{-1} C-O in alcohols and phenols; at 1237 cm^{-1}, C-O indicates stretching in esters and carboxylic acids and finally; at 861 cm^{-1} C=S stretching in thioamides. The band detected at 3273 cm^{-1} in the raw sample corresponds to stretching vibrations in an O-H group and due to strong hydrogen bonding the band is broad, an indicator of moisture in the sample. The presence of water in the raw microalgae is further supported by a very weak corresponding signal evident in the residue, as the solvent elutes much of this.

Indicators of the lipid include CH_2 asymmetric stretching bonds at 2930 cm^{-1} and symmetric 2850 cm^{-1} stretching vibrations. A CH_2 bending vibration is evident at around 1405 cm^{-1}. Ester groups are also represented by a weak C=O stretching vibration which is markedly more visible in the raw algae sample, a logical finding given removal of some of the fatty acid content as triacylglyceride (TAG) during solvent extraction. The absorption bands identified by FT-IR between 400 cm^{-1} and around 750 cm^{-1} correspond to mineral matter (a metal – halogen stretching vibration), specifically a Si-O vibration. A double metal-oxygen bond (*M*=O) and Si-O also contributes to a strong peak at around 1016 cm^{-1} in both samples.

Further in this work, the raw algae and the post solvent extraction algae residue were pyrolysed independently at a heating rate of 10^{o}C/min and the pyrolysis properties compared between the two samples. Analysis by TGA, shown in Figure 22, indicates that the *T. chui* post-solvent extracted residue initially loses weight more readily than the raw biomass sample, most likely due to the absence of inherent moisture that has been removed by organic solvent. This has the effect of reducing the amount of process energy required to initiate decomposition, at least at low temperature. However, at approximately 250°C the decomposition pathways crossover (expressed as a percentage of weight), as the lipid content retained by the raw sample begins to decompose and devolatilise quickly.

This behaviour is consistent with the second stage of devolatilisation that occurs when organic molecules in microalgae are decomposed (Shuping et al., 2010). Weight in the raw sample rapidly decreases with increasing temperature at this point and quickly exceeds that of the residue. At around 300°C the residue lags the raw sample by as much as 10% of total sample weight, before narrowing this gap to around 3% at around 340°C. As temperature increases to 500°C this gap is approximately maintained, however the weight loss trajectories then begin to steadily converge towards 700°C as all residual volatile matter is driven off.

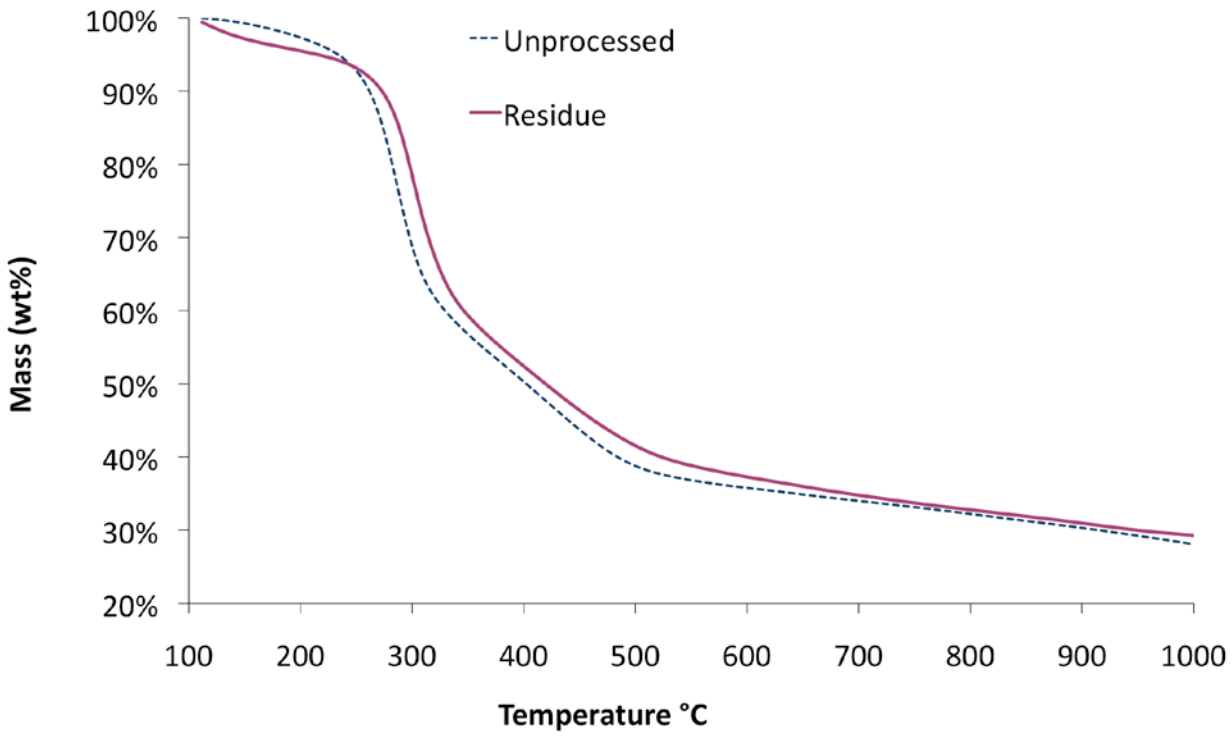

Figure 22. Mass loss from raw *T. chui* compared with mass loss from post-solvent extraction *T. chui* residue determined by thermo-gravimetric analysis (wt%)

The pyrolytic oils evolved during pyrolysis of the two samples were collected and analysed by GC-MS, while the evolved volatile gases were analysed with a micro-GC. The pyrolysis oils produced from the raw and residue samples are dominated by low molecular weight, cyclic, aromatic, and branched molecules, with some short chain fatty acids also present. The more significant peaks detected in the GC-MS chromatograms (Figure 23) for each sample are numbered and presented in Table 20, indicating those that are shared and those that are unique to each. Compound identification was again made on the basis of mass spectral matching with libraries and comparison with the literature.

The two pyrolysis oil samples exhibit some similarities in composition, albeit at varying degress of relative intensity. *Methyl 1H-indole* carries over from the natural lipid fraction to the pyrolysed raw sample and is likewise found in the pyrolysis liquid derived from the residue, suggesting that it is not decomposed at temperatures up to 500°C. *Phenol* and *methyl phenol* are present in both pyrolysis liquids (peaks III and V), a useful chemical building block of which there are already well established markets. The origins of phenolic compounds detected in bio-oil are usually associated with lignin in terrestrial plants, however in algae are believed to result from phlorotannins (Van Heemst et al., 1996).

Hymexazole (VI) was detected in both pyrolysis bio-oil samples. This compound is of interest as an agrochemical and is commonly used as a pesticide. Nitrogen containing compounds such as this are typcially markers of the breakdown of amino acids and proteins during pyrolysis. Significant differences between the two pyrolysis oils include the presence of *glycerol* and *campesterol* in the raw pyrolysis oil, largely indicative of the natural lipid component of the algae.

By contrast, an unidentified unsaturated alkanoic acid forms in large quantity through pyrolysis of both samples. This compound is characterised by a carboxyl group that is readily converted to an ester. A large peak most closely identified as *1,2-bis(trimethylsiloxy-2-(3'-trimethly-silyoxyphenyl))ethanone* is detected at a retention time of 1303 seconds in the residue bio-oil only.

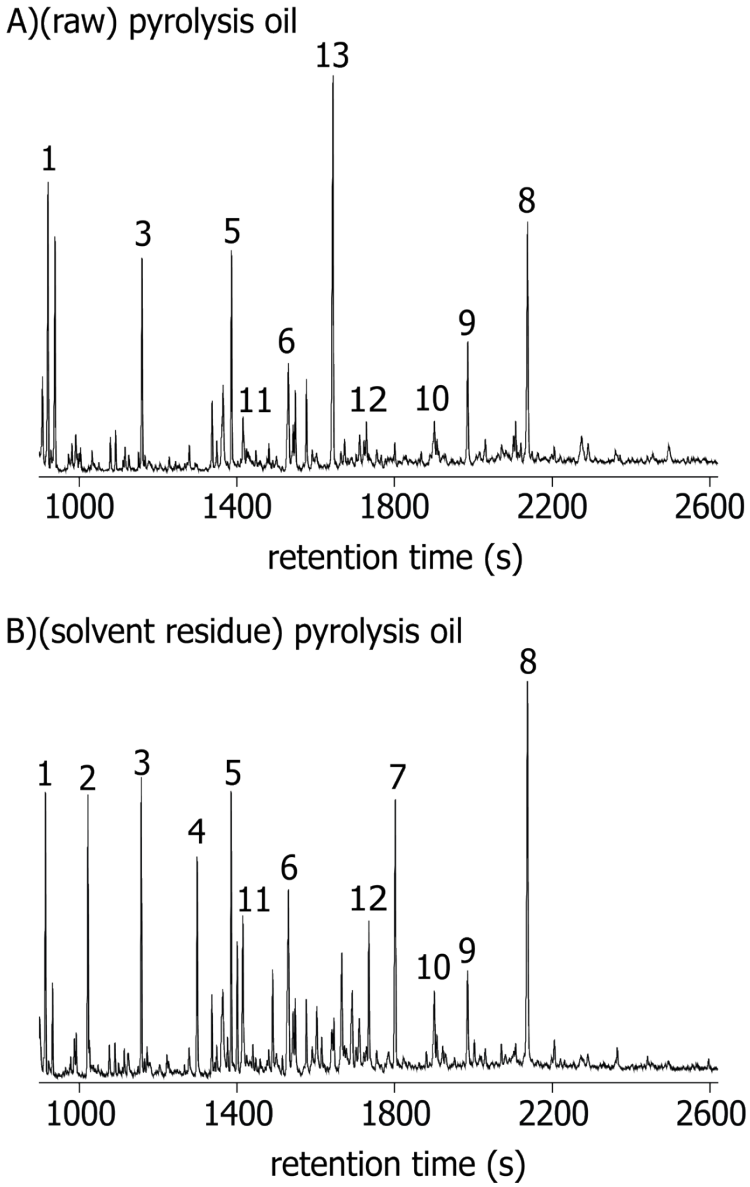

Figure 23. GC-MS spectra comparing (a) oil derived by slow pyrolysis of raw algae; (b) liquid derived by slow pyrolysis of post-solvent extraction microalgae residue (*T. chui*)

(Compounds detected: 1 = derivatising agent; 2 = silane, (2-furanylmethoxy)trimethyl-; 3 = phenol; 4 = 1,2-bis(trimethylsiloxy-2-(3'-trimethly-silyoxyphenyl))ethanone; 5 = methyl phenol; 6 = hymexazole; 7 = oxooctanoic acid; 8 = unsaturated alkanoic acid; 9 = tetramethyl quinolone; 10 = methyl 1H-indole; 11 = propanoic acid; 12 = 1,3-Cyclopentadiene, 5,5-dimethyl-1trimethylsilyl-; 13 = glycerol.)

Table 20. Natural lipid extract compared with oil species obtained from the slow pyrolysis of post-solvent extract residue (*T. chui*)

Raw	Residue	Peak #	Oil species	Retention Time (s)
✓	✓	1	derivatizing agent	915
✕	✓	2	silane, (2-furanylmethoxy)trimethyl-	1023
✓	✓	3	phenol	1161
✕	✓	4	1,2-bis(trimethylsiloxy-2-(3'-trimethly-silyoxyphenyl))ethanone*	1303
✓	✓	5	methyl phenol	1392
✓	✓	6	hymexazole	1535
✕	✓	7	oxooctanoic acid	1809
✓	✓	8	unsaturated alkanoic acid	2146
✓	✓	9	tetramethyl quinolone	1995
✓	✓	10	methyl 1H-indole	1907
✓	✓	11	propanoic acid	1420
✓	✓	12	1,3-Cyclopentadiene, 5,5-dimethyl-1trimethylsilyl-	1742
✓	✕	13	glycerol	1649
✓	✕	14	monounsaturated octadecanoic acid	3220
✓	✕	15	campesterol	4443

✓= present; ✕= absent

** inconclusive match from the database*

Analysis of the primary volatile gases evolved in each sample show differences in pyrolytic behaviour between the raw and post-solvent extracted residue samples, as shown in Figure 24. The retention of lipid in the raw sample gives rise to a greater amount of CO_2 at a peak rate of evolution of around 300°C, as the light oils in this fraction are gasified. Release of CO_2 from the post-solvent extraction residue occurs at approximately the same temperature, albeit at a lesser intensity, reflecting an absence of lipid. Since the evolution of CO_2 and CO is of a similar pattern in both samples, this suggests that a significant proportion of these gases are the result of decomposition of other components of the biomass sample, such as proteins, carbohydrates and amino acids.

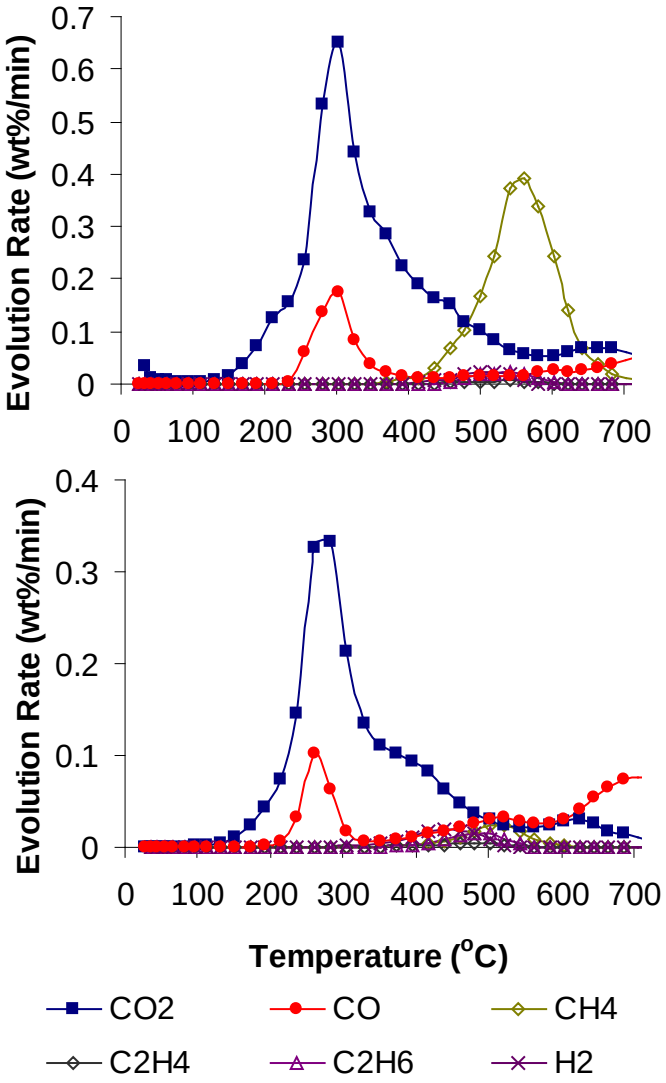

Figure 24. Evolution of volatile gases from (a) raw *T. chui* during slow pyrolysis, compared with; (b) slow pyrolysis of post-solvent extraction *T. chui* residue (wt%/min).

The other notable difference in biogas evolution relates to the emergence of methane in the raw biomass that begins at around 420°C and expands to a rate of weight loss that is approximately twenty times the rate of evolution of methane from the post-solvent extraction sample at the peak of 570°C. The differences in gas composition during pyrolysis of raw algae and post-solvent extraction residue relates to the cracking and gasification of the long-chain free fatty acids that were isolated during solvent extraction. The break-up of these acids releases CO_2 from 300°C and later, break up of the terminal methyl group that forms the end of the lipid chains. It is also possible that these methyl

groups react further with some of the available H_2 to form methane (CH_4). The net result of the absence of FFAs in the post-solvent extraction residue is that the biogas fraction has a lower calorific value overall, as less CH_4 is produced.

The ratio of oil, gas and char products observed at a temperature of 500°C also reflects the aforementioned differences in behavior observed during slow pyrolysis (Table 21). The gas yield released to 500°C by the raw sample was 9.8% by weight, considerably higher than the gas yield derived from the post-solvent extracted residue (4.9wt%). The char production observed between the two samples was the same, with around 38.8 wt% in each. Finally, the amount of pyrolytic liquid was found to be 5.0% higher in the residue compared to pyrolysis of the raw sample, at 56.4wt%.

Table 21. Comparison of evolved liquid, gas and char ratios derived from slow pyrolysis of unprocessed *T. chui* and post-solvent extracted *T. chui* residue (500°C)

Species	**Char (wt/%)**	**Gas (wt/%)**	**Liquid (wt/%)**
T. chui – unprocessed	38.8	9.8	51.4
T. chui – post-solvent extracted residue	38.7	4.9	56.4

Notably, in the case of the solvent residue by-products, these percentages should be adjusted to reflect the percentage of the upstream biomass feedstock in order for proper comparison of evolved product ratios to be made. As shown in Figure 25, the ratio of gas, char and oil derived from the residue equates to 4.2%, 33.0% and 48.2%, of the starting weight respectively. Furthermore, the pyrolysis liquid fraction derived from the residue is likely to contain less water due to the dehydrating effect of the prior solvent extraction (although water can also be reformed as a product of secondary reactions). Hence, the bio-oil component and energy density is likely to be higher again as a proportion of the liquid fraction, in addition to being greater in volume than the total liquid fraction derived from direct pyrolysis of the raw biomass.

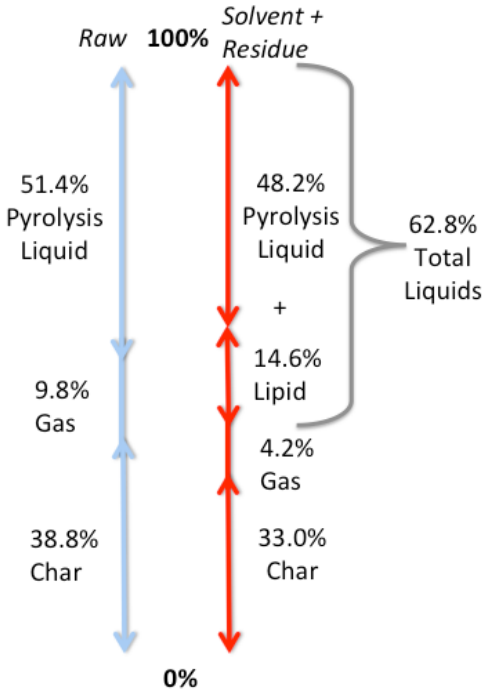

Figure 25. Comparison of evolved pyrolysis products and their ratios from raw *T. chui* versus post-solvent extraction *T. chui* residue (wt%).

Overall, a 2-step combination of solvent extraction of natural lipids from microalgae biomass (which may in time be replaced by an alternative, equally efficient and optimised process), combined with slow pyrolysis of the residue, could yield more than 11% more oil product overall on a dry weight basis, compared to pyrolysis of raw algae, due to the nature of the thermo-chemical decomposition process (Figure 25). The nature of the solvent extraction process is such that it has the added benefit of removing moisture from the biomass and extracts high value chemical compounds. While industrial use of organic solvents raises concerns about environmental impact and toxicity, these can theoretically be captured, recycled and re-used as part of a stewardship system, and thus their impacts managed.

5.4 Conclusion

Extraction of the natural lipid fraction found in *T. chui* presents an opportunity to recover a high-value product directly from a dried microalgae biomass sample. This work found that for *T. chui*, in which the natural lipid fraction is polar in nature and consists primarily of fatty acids, use of neat SC-CO_2 for lipid removal is likely to be ineffectual. Co-solvent extraction with SC-CO_2 produces an improved result, however further refinement and testing of SC-CO_2 processing parameters and methods with this species is required. Accelerated solvent extraction (ASE) using DCM:MeOH in a ratio of 9:1 showed the largest natural lipid extraction from the studied microalgae species at almost 15 wt/%.

The bio-oil production yields could be further maximised by pyrolysis of the post-extraction residue. The oils resulting from pyrolysis of the post solvent extraction microalgae residue were found to be of similar composition to those produced through pyrolysis of raw microalgae, albeit with minor differences that appear to reflect the presence or absence of quantities of natural lipid in the raw microalgae sample. This study demonstrates that the combination of a two-step lipid extraction and slow pyrolysis processing regime can yield an oil product high in valuable fatty acids in the first instance, in addition to increasing the total amount of oil yield produced overall when combined with slow pyrolysis processing. This can be achieved without greatly affecting char yield, though the calorific content of the equivalent biogas fraction is reduced commensurate to the preservation of the natural lipid.

Subject to the techno-economic feasibility and life cycle profile of a scalable system, a two-step lipid extraction and pyrolysis regime may further support the commercial viability of microalgae cultivation and processing through diversification of the product value chain. Ultimately, this maximises retention and production of bulk oil product, whilst maintaining higher rates of unit area biomass productivity through cultivation of select microalgae species.

Chapter 6: Life cycle assessment of a microalgae biomass cultivation, bio-oil extraction and pyrolysis processing regime

Original manuscript published in Algal Research, 2013, 2 (3), pp 299-311

6.1 Introduction

Life cycle assessment (LCA) of microalgae biomass to biofuel and bio-product conversion is of great importance to enable viable technological innovation, with reduced energy intensity and improved overall environmental performance. Numerous LCAs have been undertaken in the past aiming to evaluate the microalgae biomass to biofuel and bio-product prospect on a conceptual level, based on a variety of assessment methods and approaches (Chisti, 2008; Lardon et al., 2009; Batan et al., 2010; Clarens et al., 2010; Jorquera et al., 2010; Sander & Murthy, 2010; Campbell et al., 2011; Collet et al., 2011; Pfromm et al., 2011; Soratana & Landis, 2011; Yang et al., 2011; Handler et al., 2012). However, across the existing LCA studies, there is little common ground in relation to goal and scope, system boundaries, functional units and life cycle impact assessment (LCIA) methods, making comparison of the various emerging and competing cultivation, harvesting, processing and product pathways difficult (Liu et al., 2012).

Arguably, the most comprehensive approach to LCIA of microalgae systems published to date relates to the work undertaken by the Argonne National Laboratory in the United States that has focused on production of liquid transport fuel substitutes (Frank et al., 2011). This has resulted in the application of the Greenhouse Gases, Regulated Emissions, and Energy use in Transport (GREET) 'well-to-wheel' model for comparison of algal biofuels (notably produced through direct lipid extraction) with conventional petroleum-based transport fuels, providing a common basis on which assessments of various algal biofuel pathways can be made. This approach is useful and well designed for the purposes of assessing biofuel production however the study is focused on downstream performance of fuels in combustion engines only and is limited to environmental metrics commonly associated with vehicle emissions and performance.

The microalgae biomass, biofuels and bio-product industry is currently trying to achieve expansion to deliver a broad range of products, from agri-/aquaculture feed and omega 3/6 fatty acids, to biofuels and biochar, where multiple products may need to be considered through an often complex value chain. Therefore, it should be expected that end-product and process transparency, in addition to having an ability to consistently and simultaneously assess a range of co-products and report across a comprehensive set of environmental impact categories, will be required at some point. A common LCIA method that is generically applicable to all algae biomass applications would enable consistent and valid comparability of results both within and outside the industry and assist in more accurately assessing co-product outcomes.

Since full commercialisation of microalgae for energy products in particular is still in development, many LCA studies rely on either laboratory scale or pilot technology, incomplete data, or subjective assumptions, and few have taken a wide-ranging approach to benchmarking or environmental impact assessment (Collet et al., 2011; Lardon et al., 2009). A complicating factor is that there are many possible options to consider in progressing through cultivation, harvesting, handling, extraction and/or conversion, in order to produce a broad range of potential by-products, and no preferred route(s) have yet emerged. A 'Technology Roadmap' published by the US Department of Energy's (DOE) Biomass Program collected the major streams of research and commercial endeavour in relation to algal biofuels into a single, integrated overview (2010b). A clear message that emerges from this report is that standardisation and comparison of LCA results will be challenging, as different product pathways may require unique assumptions, functional units and/or allocation decisions.

Selection of a specific algae cultivation and processing pathway depends on a number of inter-related factors, including:

1. practical limitations associated with geographic proximity to nutrient, water/wastewater and/or carbon dioxide inputs
2. additional geographic parameters such as climate and land use

3. identifying suitable sites that determine whether or not it is a marine or freshwater species to be cultivated
4. species selection, that narrows the downstream products that can be feasibly derived, based on biochemical profile
5. the preferred processing route chosen, as directly linked to the identification of desired (and commercially viable) downstream products

At present, there is no known LCA study within the current body of published work that assesses the pyrolysis conversion of microalgae biomass into its various co-products. The LCA model presented here is based on industrial-scale cultivation of microalgae biomass on a theoretical 80 ha farm, coupled to a downstream slow pyrolysis process that produces renewable bio-oil, biogas and biochar.

Slow pyrolysis is selected as a prospective method for achieving large-scale biological carbon capture and storage (bio-CCS), through carbonization of high volume microalgae biomass to produce biochar that can be added to soil, a process of effectively 'sequestering' carbon (Lehmann & Joseph, 2009). Some of the carbon in biochar is labile and will continue to partake in the carbon cycle through the action of soil microbes and plants. However, research indicates that a portion of the carbon is also stabilized in a matrix that resists degradation and that may well stay relatively unchanged for many hundreds, if not thousands, of years (Roberts et al., 2009). The long term carbon abatement benefit of microalgae biochar has been previously estimated at around 9% by weight of the input *Tetraselmis chui* microalgae feedstock (Grierson et al., 2011b). Hence, this analysis serves as a means to assess this emerging opportunity at industrial scale, both in terms of volume and broad environmental impact, and to compare it with various co-product scenarios.

6.2 Research Methods

6.2.1 Modelled process

The microalgae species used as the basis for this LCA is derived from the monoculturing of *T. chui*, a hardy, marine unicellular microalgae commonly used in the aquaculture

industry (Brown, 1991). The projections for performance of mass cultivation of *T. chui* are based on successful, small-scale experience with this species at hatchery scale (up to 1000L of growth medium) that has been described in previous work (Grierson et al., 2009; Grierson et al., 2011a; Grierson et al., 2011b). In addition, successful cultivation and harvesting of multiple microalgae species to date using a 49.5 kL closed photobioreactor (PBR) design and harvest system developed at James Cook University in Townsville, Queensland, under the Advanced Manufacturing Co-operative Research Centre (AMCRC), has further informed the LCA model.

A schema featured in the DOE Roadmap document (Exhibit 10.1, *High level illustration of various approaches and pathways to developing algae-derived biofuels and co-products,* pg. 93), was the basis of the processing and co-product pathways investigated in this work, as presented in Figure 26.

6.2.2 LCA Method

LCA modelling was carried out using the PhD version of SimaPro 7.3 software provided by Life Cycle Strategies Pty Ltd, Australia. As per the ISO standard, the structure of this LCA is based upon an iterative 4-part process of defining goal and scope; building an inventory of resource, emission and energy flows; application of an impact assessment method; and interpretation of the study and results.

The LCA was specifically conducted in accordance with the Building Products Innovation Council (BPIC) methodology (2010a; Bengtsson & Howard, 2011) because it provides:

- a consistent level playing field methodology
- an independent, authoritative and recognized basis for product comparisons,
- alignment with the broader Australian Life Cycle Inventory (AusLCI) project (2013)(2013)(2013) (Australian Life Cycle Assessment Society, 2013), and
- Compliance with ISO14040/44 for international recognition.

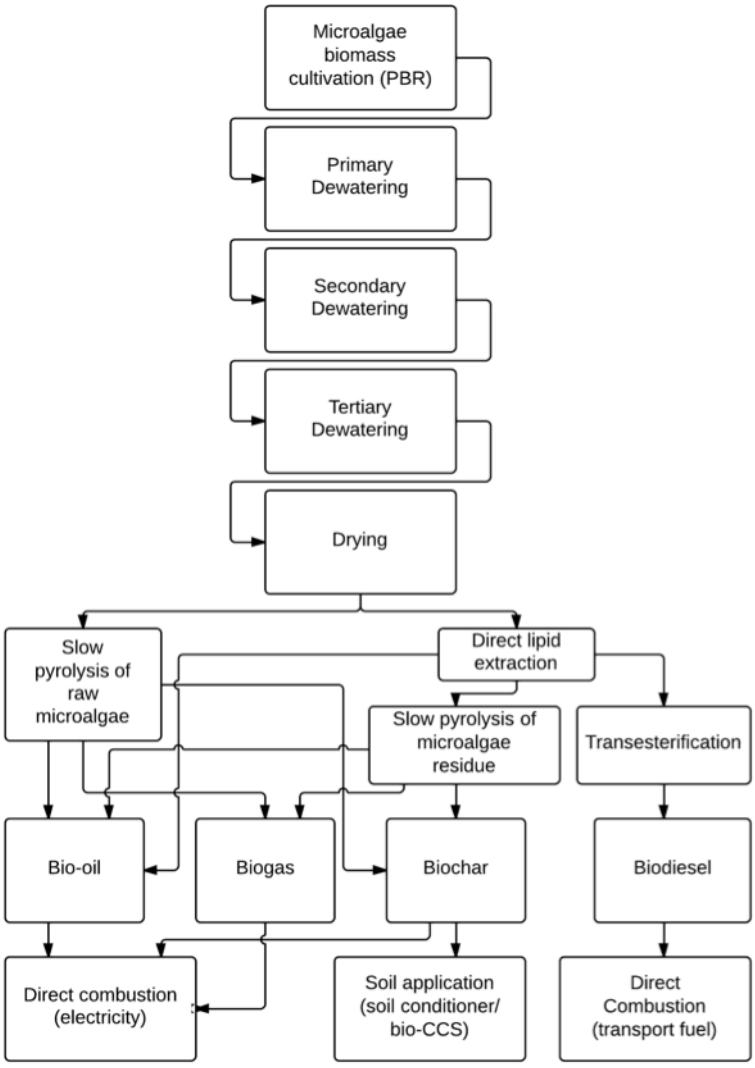

Figure 26. Value chain diagram comparing pathways to end products and applications in a microalgae biomass and slow pyrolysis processing regime

6.2.3 Goal and Scope

The following information on Goal and Scope is assembled in accordance with the ISO 14040/44 standards.

LCA Goal

- To model the environmental impact of an integrated microalgae biomass cultivation and pyrolysis processing value chain on an industrial scale.

- To put forward a standardised life cycle model for assessment of microalgae systems.
- To establish a performance benchmark against other microalgae value chain pathways that can be measured through the application of a common ‘level playing field’ LCIA methodology currently in use by other industries.
- To use these results to inform prioritisation of process innovations.

System Boundaries

- The system is modelled for the geographical location of Queensland, Australia and is based on fictional, annualised production on an 80 ha microalgae farm.
- Cradle-to-grave environmental impacts of microalgae systems and products are considered, broken down into four discrete stages, including:
    - Cultivation (to harvesting gate)
    - Harvesting (to processing gate)
    - Processing (to retail gate)
    - Products (including utilisation/consumption)
- Operational energy, water, carbon dioxide (CO_2), and nutrient requirements are treated as system inputs. Captured CO_2 emissions are burdened only with the energy impacts associated with delivery of flue gas to the microalgae farm.
- A logical distinction is made for the purposes of this study between short-lived, degenerative infrastructure (i.e., with a relatively short life span due to operation of the plant) versus permanent fixed infrastructure that has an impact that can be amortised over the entire 30-year design life of the plant. Low Density Poly Ethylene (LDPE) required for manufacture of PBRs has an assumed operational life of only 5 years, hence its impact is a significant factor over a single year of operation. The 5-year expected lifetime is purely an assumption based on observation of this PBR system over a 2-year operational period and constitutes a reasonable assessment of expected working life, based on experience.

Excluded from the system boundary are:

- Solar radiation provided free to a phototrophic cultivation system.
- Site levelling works (land occupation is accounted for)
- Capital infrastructure, such as plumbing, pumps, sheds, processing plant and machinery. While a detailed model of the infrastructure required to support an integrated, multi-stage microalgae farm and processing plant itself has not been built for this study, a proxy guide from the Ecoinvent life cycle databases is able to indicate whether this is likely to be of material impact (Hischier et al., 2010). Given a projected design life of 30 years, the indications are that the overall impact when spread over the operational life can be expected to have an annual impact of <3% on the overall environmental impact score (measured in Ecopoints), regardless of the end product scenario. Further detail regarding the underlying assumptions and calculations here is captured in the Supplementary Information (Appendix B).

Environmental Impact Categories

The BPIC impact assessment method (Bengtsson & Howard, 2011; 2010a) has been adopted in this work given its success in Australia in helping to establish an industry-wide, AusLCI-compliant, 'level playing field' standard for a wide range of products, which reports on 15 distinct mid-point environmental indicators (Figure 27). Several categories (shown in black in Figure 27) have been omitted in this study as Indoor Environmental Air Quality, and Noise & Nuisance are not considered relevant for microalgae biomass systems. Soil Salinization has previously been proposed in relation to irrigation practices in Australia where salinity is a major issue (Feitz & Lundie, 2002), however as a potential impact category, no LCIA methods could be found that currently incorporate this indicator hence no impact could be reported. Given the nature of biochar, especially that derived from a marine biomass feedstock such as microalgae, this is acknowledged as a gap that is arguably of relevance to any biochar study. This category is highlighted here and is notable for its absence from the available library of methods.

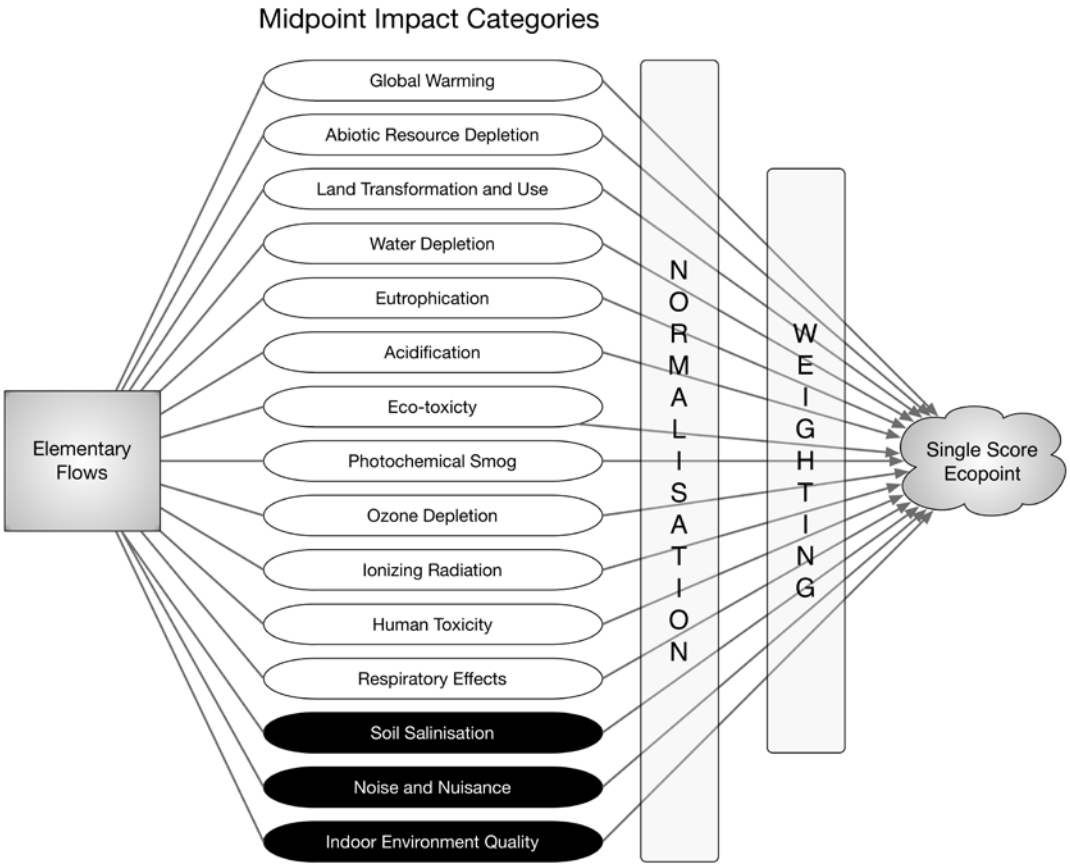

Figure 27. The mid-point environmental impact categories adopted in the BPIC/ICIP study

The remaining 12 environmental impact categories and characterisations have been used in this project and are amended with updated toxicity methods, noting that the choice of generic USETox (Hauschild et al., 2008; Rosenbaum et al., 2008) characterisation factors rather than Australian toxicity factors (Lundie et al., 2007b) was adopted to increase international relevance of the results:

I. Global warming: characterised in 100-year global warming potential factors (GWP100) for carbon dioxide equivalents (kg CO_2-eq).
II. Abiotic resource depletion (excl. water): As promoted by the Institute of Environmental Science, University of Lieden (CML), version 2 baseline 2001 relative characterisation factors for abiotic resource depletion potential re-normalised to be measured in the reference unit oil equivalents (kg oil-eq) for non-renewable fuel depletion and iron

equivalence (kg Fe eq) for mineral depletion instead of antimony equivalence used by the CML (Huppes, 2002).

III. Land transformation and use: characterised in hectare years (ha a) using the Australian Impact Assessment Method provided in the Australian version of SimaPro. Although algae cultivation systems notionally will occupy arid, non-arable land, this category is reported to provide a basis for comparability with competing biomass feedstocks.

IV. Water resource depletion: characterised using total freshwater consumed (kL water) as per the Australian Impact Assessment Method provided in the Australian version of SimaPro.

V. Eutrophication: CML 2 baseline 2001 characterisation factors in phosphate equivalents (kg PO_4 eq).

VI. Acidification: ReCiPe (Wegener Sleeswijk et al., 2008) global (H) midpoint characterisation factors in sulphur dioxide equivalents (kg SO_2 eq).

VII. Eco-toxicity: USETox (Rosenbaum et al., 2008). The characterisation factor for aquatic ecotoxicity (ecotoxicity potential) is expressed in comparative toxic units (CTUe) and provides an estimate of the potentially affected fraction of species (PAF) integrated over time and volume per unit mass of a chemical emitted (PAF m^3 day kg^{-1}).

VIII. Human toxicity: USETox (Rosenbaum et al., 2008). The characterisation factor for human toxicity (human toxicity potential) is expressed in comparative toxic units (CTUh), providing the estimated increase in morbidity in the total human population per unit mass of a chemical emitted (cases per kilogram).

IX. Photochemical smog: ReCiPe (H) global midpoint characterisation factors in non-methane Volatile Organic Compound (VOC) equivalents (kg NMVOC eq).

X. Ozone depletion: World Meteorological Organisation (WMO) method (2007b) for characterisation in Chlorinated Fluorocarbon 11 equivalents (kg CFC-11 eq).

XI. Ionising radiation: ReCiPe (H) global midpoint characterisation factors in Uranium 235 equivalence (kg ^{235}U eq).

XII. Respiratory effects: IMPACT 2002+ expressed in particulates with a diameter of 2.5 μm equivalence (kg PM2.5 eq) (Jolliet et al., 2003)

Characterised environmental impacts are normalised, weighted and aggregated into single score ‘Ecopoints’ using the BPIC LCIA method, where 100 Ecopoints represents

the average annual environmental impact of an Australian resident (2011c). Normalisation and weighting factors are provided as Supplementary Information to this work (Appendix B).

Functional Units

There are two primary functional units used (MJ and t) to provide a clear basis for articulation of four possible end-use product applications. Hence, the following in relation to each product are considered in this study:

- **1MJ of pyrolysis biogas** combusted for electricity
- **1MJ of pyrolysis bio-oil** combusted for electricity or extracted lipid refined for transport fuel
- **1MJ of pyrolysis biochar** combusted for electricity
- **1t of pyrolysis biochar** applied to soil as conditioner

It is important to have all of these options identified distinctly, as the intent is not to compare the various extracted and pyrolysis co-products against each other. Rather, this approach provides the means to benchmark each against their incumbents in the applicable product category (e.g., biogas vs. natural gas, bio-oil vs. heavy fuel oil, etc.) on a 'functional equivalent' basis.

1t of dry weight (DW) microalgae biomass (cradle-to-harvesting gate, incorporating the cultivation step only) is also briefly considered as a starting point, which enables comparison with various competing cultivation technologies and alternative biomass feedstocks.

Allocation Procedure

Both the reference methodology used in this LCA and AusLCI (Grant, 2012; 2010a) mandate that economic allocation be consistently applied for multi-output processes where it cannot be avoided or system expansion applied, with a view to comparability of

results across a range of products and services. Economic allocation effectively means that the proportion of environmental burden carried by multiple by-products of a process is attributable to their economic (market) value and this approach is now well established (Guinee, 2002; Bauman & Tillman, 2004; Guinee et al., 2004; Pears & Grant, 2005; Lundie et al., 2007a; BSI, 2011). Environmental impact is ultimately fully allocated across the various co-products, however "the extent to which each product or service contributes to the economic return from operation of the process(es) is…the most appropriate unit that can be used for consistent allocation" across the full scope of products/services in the economy (2010a). Although LCA results are impacted by time averaged commodity price data availability and quality, economic allocation is still a relevant choice when a key objective is to achieve consistency up and down the supply chain, which is essential for a level playing field assessment methodology.

The following assumptions regarding retail prices for end products in this study were used ($AUD):

- **Electricity – Queensland** (2012a) $29.07/MWh
- **Biodiesel – based on petroleum diesel** (2012b) $1.52/L
- **Biochar** $50/tonne

These prices are reflected in the economic allocations tabled in the Supplementary Information (Appendix B), according to each (co-)product, end-use scenario. Notably, a mature market for biochar has not yet emerged, hence its price cannot be reliably determined – this figure is a mid-range estimate (assuming a carbon price) based on published data (Brown et al., 2011; Galinato et al., 2011). All LCA results are tested against sensitivity to biochar prices.

In the case of microalgae cultivation systems, waste products used as process inputs, such as nutrient or wastewater have no positive economic value (given that they would otherwise incur an economic cost to treat) and therefore they inherit no upstream environmental impacts. Likewise, in the case of CO_2, a Federal carbon tax of AUD $23

per ton emitted has applied in Australia from July 1, 2012 hence its utilisation for algae cultivation is rather an avoided cost.

Data Sources

- Material and energy inputs, and process innovations are based on a fictional engineering design, leveraging existing technology insights where relevant. Additional insights and fundamental data are based on experimental work and field trials carried out by the authors.
- The veracity of individual numbers is obviously a function of the quality and reliability of their source. In a value chain of this complexity, acknowledged as being based partly on known fundamentals and partly on theoretical projections/assumptions, only sensitivity analysis can highlight the aspects of the study that are material to the outcome (regardless of the source). Note that in the LCI tables provided in the Supplementary Information (Appendix B), a designation for each data source reflects its place in the order of data preference.
- Cradle-to-use life cycle inventory data is based on (in order of preference):
    - Published experimental data relating to the thermal and chemical properties of *T. chui* microalgae
    - Unpublished field data provided by industry collaborators
    - Published LCI/LCA studies relating to microalgae systems and products
    - AusLCI datasets provided with SimaPro v7.3
    - The Australasian LCA database provided with SimaPro v7.3
    - International data from the Ecoinvent (v2.2) database, adapted to Australian conditions, as required
    - Derivation, estimation or assumption based on best available data or closest match

Value choices

Although CO_2 supplementation is considered necessary for all commercial microalgae systems, the precise industrial source and environmental burden of this CO_2 is deemed irrelevant for LCA purposes. From an environmental impact perspective, there is no

effective limiting factor on the availability of CO_2 derived from fossil resources that would otherwise be discharged to the atmosphere and hence it can be considered to be of negligible value considering its oversupply, relative to actual industrial demand (2011a). It is however important to account for the process of CO_2 delivery to a microalgae cultivation facility as gas transport is an energy intensive process directly attributed to this activity.

A reasonable assumption made in this study is that the CO_2 used for algae cultivation is sourced from the flue gas taken post-scrubbers that are designed to remove particulates and to achieve desulphurisation in coal-fired power stations, as required by Australian (in this case, Queensland-state) legislation (2008). Heavy metals present in the flue gas mix will end up in the algae biomass due to their sorption capacity (Klimmek et al., 2001; Mehta & Gaur, 2005; Sandau et al., 1996) and subsequently, these will be further concentrated in the biochar fraction as ash (Grierson et al., 2011b; Özçimen & Ersoy-Meriçboyu, 2010; Strezov et al., 2007). However at this point such levels in the biochar product are still only a small percentage of soil investigation levels for health and ecological contamination and are not considered relevant to this study (1999).

Data Limitations

Scaled construction and operation of an 80 ha microalgae farm is based on a fictional engineering model only. Material and energy inputs for transesterification of algae oil into biodiesel are based on Ecoinvent library or published data (Batan et al., 2010). Actual combustion of the candidate microalgae strain or its pyrolysis by-products for electricity or transport fuel markets has not been undertaken hence these end use unit processes and values are assumed based on their closest logical proxy listed in the Ecoinvent databases. In this study, pyrolysis bio-oil (27.9 MJ/kg) is assumed to be a functional proxy for Heavy Fuel Oil (HFO – 41.2 MJ/kg), with a 33% adjustment made due to a lower HHV. This effectively means that an additional quantity is required for combustion to achieve the same functional outcome (in terms of electricity output, for instance). Pyrolysis biogas (2.9 MJ/kg) is likewise assumed to combust similarly to landfill gas (25 MJ/kg), albeit it is far less energy dense and adjusted to only ~11% of the HHV. Finally,

combusted biochar (14.5 MJ/kg) is equated with brown (thermal) coal (14.7 MJ/kg) given its similar HHV. Adjustment is also made for generation plant, with allowance for efficiency of combustion of all fuels ultimately equating to an aggregated figure of electricity 'sent out' into the grid. Otherwise, when allocating for electricity under all scenarios there is no accounting for co-products of power generation such as fly ash as it is not possible to establish if these could be recovered at economic rates.

Despite the fact that this microalgae farm concept has yet to be constructed on an 80 ha scale, many of the sub-processes and systems are based on small-scale field trials of actual technologies, as well as operational data.

Undoubtedly, there is considerable room for general optimisation and innovation of this value chain, and the veracity of the model cannot be borne out without detailed engineering design and subsequently, continuous, scaled operation of the farm itself and testing of derived products. Nevertheless, this study aims to present indicative implications of achieving industrial scale based on pilot experience with various technologies, and where possible, presents a model that is based on best available data. It is ultimately designed to inform a continuous improvement process in the design of an industrial scale microalgae value chain made up of many integrated components.

Data Quality Requirements

Now that the scope, goals, and data sources that will be used have been outlined, we briefly discuss the criteria used to determine what will be included or excluded in the final results.

- Time related coverage: an assumed 1yr of microalgae farm operation. Data as close as possible to known system performance, integration of existing technologies, growth performance under cultivation and thermo-chemical decomposition behaviour.
- Geographical coverage: Queensland, Australia (Queensland average)
- Technology Coverage and Completeness: All major components of the microalgae farm system (as defined above) are included in accordance with a modelled

engineering design. Downstream implications and behaviour of products during use are less well known for the most part since the end products have not yet been manufactured and tested by the authors (e.g., algae biodiesel), with existing proxy data from analogous products substituted to find the closest logical fit.

- It is common practice in LCA/LCI protocols to propose exclusion limits for inputs and outputs that fall below a stated % threshold, but with the exception that where a small input/output has a “significant” impact it should be included. The procedure for modelling minor process flows is herein adopted whereby sensitivity analysis is used to test the dependence of the final impact assessment to certain inputs/outputs. This is done by changing individual inputs; by doubling and halving each data item, and observing the change to the overall impact. Provided that the final environmental significance for the product varies by less than 10%, approximate values can be used. Where the variation is greater than 10%, further investigation of this parameter should be undertaken.
- Representativeness: Data from a specific process and company.
- Reproducibility: The systems shall be modelled and described in a manner that allows for reproduction of the study/results.
- Uncertainty of the information: Primarily relates to an absence of any long term operational and maintenance data over a continuous period of 12 months or more (e.g., to assess reliability of systems, influence of biological contaminants, shutdown/maintenance times, component technologies, etc.).

6.2.4 Life Cycle Model

This work reflects a sequence of 4 discrete life cycle stages, each containing a series of sub-processes and/or variants within it (Figure 28). The major difference in this model in relation to the US DOE approach is that it models the cultivation and harvesting stages separately, providing the ability to benchmark and compare distinct technical options for each. LCI data, broken down by processing stage and end-use scenario is presented as Supplementary Information (Appendix B).

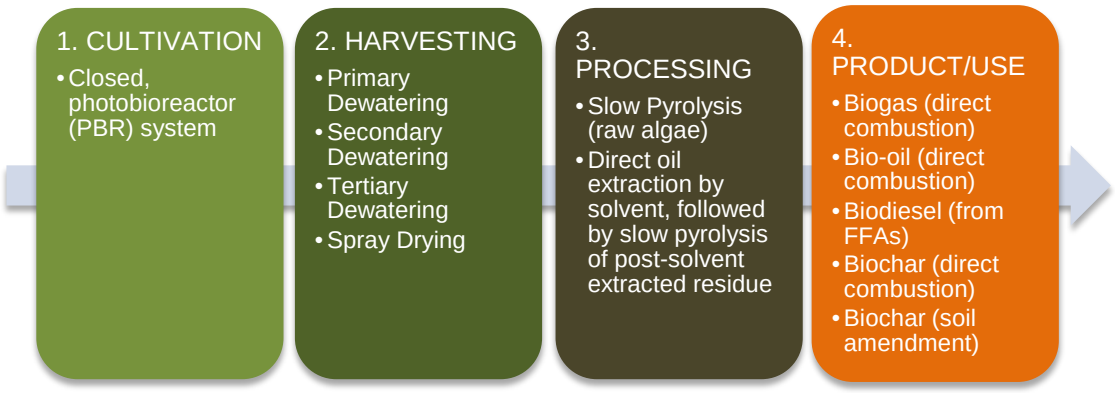

Figure 28. The major life cycle stages considered in this study, including their various nested unit processes

Cultivation

A hypothetical microalgae farming system of 80ha (200 acres) located near the coast in central Queensland, Australia, is the reference scale and design on which this analysis is constructed. The microalgae farm concept entails a conceptual, modular network of linked photobioreactors (PBRs), into which process water, nutrient, culture inoculum and CO_2 (in flue gas) is supplied, all connected to a single, centralised inoculation, harvesting and processing plant. CO_2 as a component of the flue gas stream (13%) is sourced from an adjacent power station and dissolved within the growth medium using a Speece Cone design (Speece, 1972). While 13% CO_2 is a very high proportion of gas relative to the 1-5% CO_2 enriched mixture typically used in intensive algae cultivation (Jaworski et al., 1981; Hailing-Sørensen et al., 1996; Qiu & Gao, 2002), once dissolved in the growth medium with this technique it is more important to regularly monitor flow and volume to ensure that an adequate supply of carbon is maintained to the culture, while simultaneously monitoring pH (Negoro et al., 1992). Nutrients are likewise added to this medium, prior to delivery to the cultivation system. Excess nutrients present in the water column are recycled along with the process water recovered during the various dewatering cycles (which is returned to the cultivation system).

The *T. chui* culture is modeled based on growth in 50m long, tubular plastic (LDPE) PBRs, each occupying an area of non-productive, graded land, with suitable allowance made in the overall site plan for access, maintenance and provision of services (Stammbach et al., 2011). A mechanical culture suspension method consisting of a sled that moves up and down a fixed cable operates intermittently for a total of 6 h during the daytime, helping to prevent settling of culture and ensuring that the *T. chui* cells are exposed to a regular light-dark cycling of solar radiation in order to maintain photosynthetic activity, without inviting photo-inhibition. This suspension method incurs an operational power burden and is incorporated into the LCA model also.

An evaporative cooling effect is provided by a fan in each 50m PBR that also keeps it inflated for 12 h a day, maintaining the temperature of the growth medium within an acceptable maximum daytime range and negating the need for any extensive physical support structure. Daytime evaporative losses from the cultivation system were measured and found to represent 566 L/day as an average over four consecutive days of operation (approx.1.1%/vol). Notably, the precise amount of water lost will vary with temperature and humidity at different times of the year, however this figure is taken as a reasonable estimate for the purposes of the model.

At this rate of evaporation per PBR, operated for 365 days per year, the entire cultivation system would require a make-up volume of fresh water amounting to 925.52 ML per annum. Together with annual evaporative losses from the spray dryer (33 ML), water vapour leaves the cultivation and spray drying steps as an emission to air and must be replenished, in order to control the salinity and overall volume of growth medium.

Harvest or ‘strike’ density in the culture is assumed to be ideal when the *T. chui* cells are in the latter stages of the exponential growth phase, when it is achieving a stable yet robust rate of reproduction. The algae are removed from the PBRs in suspension at a density of 1g/L as a continuous ‘trickle harvest’, representing approximately 13.3% of the total volume of the system turned over each day. Sensitivity analysis of the daily productivity of the culture is applied in this study to evaluate the impact on total daily farm yields, and thereby the intensity of environmental impact from a life cycle perspective.

Harvesting

The harvest cycle consists of a series of dewatering and drying steps that are designed to progressively concentrate the microalgae biomass to the point at which it can be processed, based on actual data collected at James Cook University in Townsville, Queensland. Primary harvesting consists of an initial electro-flocculation step that is able to exploit the negative charge of microalgae cells, causing them to aggregate. This does not increase the concentration of cells relative to the growth medium as such, rather it makes the subsequent step of separation considerably easier (Xu et al., 2010; Poelman et al., 1997; Aragon et al., 1992). The electrodes in this unit are known to leach a minimal amount of iron into the water during this process however this is expected to be immaterial to the results and no additional chemical or biological coagulant is utilised.

A secondary harvesting process uses dissolved air floatation (DAF) to concentrate the algae by a factor of approximately 18.4 times into a thick mat that is mechanically removed from the surface of the growth medium. This concentrate is then passed into a tertiary dewatering stage - a centrifuge - wherein a spin cycle further concentrates the algae by an additional factor of 15.6 times, to approximately 28.6% solids content with only minimal extracellular water present (<3%). All growth medium separated out during the various dewatering stages is captured and returned to the cultivation system. This recycles conditioned process water and excess nutrients (including carbonate), in addition to reintroducing the small quantity of microalgae culture that can be expected to evade the harvest process.

The algae paste that comes out of the centrifuge unit is passed into a highly efficient industrial spray dryer, where water is vaporised at an air intake temperature of 200°C and separated from the biomass, leaving behind a dry powder product ready for pyrolysis (5% moisture). At around 80% moisture, Kajiyama et. al. (Kajiyama & Park, 2011) found that the process energy requirements to achieve complete evaporation of moisture from material using this technology is around 4 GJ/t of input slurry. Another study of a range of industrial spray dryers in the UK placed the average unit at an energy consumption rating of 4.87 GJ/t of feed-in slurry, with the most efficient dryers in use somewhere in the range of 3.0-3.5 GJ/t (Baker & McKenzie, 2005).

Spray dryers typically operate at inlet temperatures of around 200°C, which could enable a considerable amount of both sensible and latent heat to be recovered from the exhaust. One company fitting heat recovery systems to spray dryers claims an energy saving of 25% can be achieved by pre-heating the inlet air directly from the exhaust (2012c). Another study suggests that 42,000 KWh is needed to vapourise 13,000 gal of water from a 10% algal solids concentration at 70% efficiency, from which up to 70% of process heat could effectively be recaptured as steam, thereby reducing the net energy input required to achieve vapourisation to a balance of 30% (Sturm & Lamer, 2011). Furthermore, a US DOE report found that use of heat exchangers employed for low temperature heat recovery from flue gases presents an opportunity to capture and pre-heat air in a coal-fired power station to deliver overall efficiency improvements in generation of up to 3%, where flue gas is cooled from 150°C – 60°C prior to desulphurisation (Johnson & Choate, 2008).

Large-scale engineering and retrofit of integrated heat recovery systems for power stations can be complex but are likely to be a significant lever for algae value chain efficiency, where a dry biomass product is desired (i.e. for pyrolysis) and thereby, for bio-CCS using algal biochar to be considered. Suffice to say that while spray drying itself is very energy intensive, there is ample opportunity in many power stations for co-located heat recovery and/or energy efficiency measures to be engineered to either directly feed into or offset the energy requirements for spray drying.

Given technical advances and the need to optimise for relatively high efficiency in order to achieve commercially viable production, 4 GJ/t of evaporated water is assumed as the thermal energy requirement in this work. As the latent heat for evaporation of water is measured at 2.25 GJ/t, this assumes a design efficiency of around 56%. At 72.4% moisture content with an intent to spray dry to 5%, this requires that 674 kg of water per tonne of feed-in slurry must be vaporised, in order to yield 286 kg of dry algae. Put another way, the total amount of energy needed to deliver 1 tonne of spray dried algae using this method based on the starting solids concentration would be 14 GJ (notably, this represents 86.9% of the HHV of the microalgae biomass itself without any heat recovery or energy efficiency taken into account). In the process this would vapourise

2,359L of water that, later cooled to the point of condensation, would release an equivalent amount of heat.

For the purposes of the LCA model, a net drying energy requirement for microalgae of 4.2 GJ/tDW in preparation for pyrolysis is assumed based on 70% heat energy recovery and/or efficiency measures, with the sensitivity of results to this parameter later tested. The shortfall in thermal energy input is made up by electricity at a conversion of 3.6 GJ/MWh, which in this case amounts to 1.2 MWh for each tonne of dried microalgae produced. At a feed rate of 1 kg of microalgae slurry per second into the spray dryer, 2426.4 kg of water would be vapourized per hour at an energy burden of 9.7 GJ/hr to derive a product ideally suited for pyrolysis. This is the equivalent of 2.7 MWh, or around 5.8 s of generation at Queensland's 1680 MW Gladstone Power Station when operating at full capacity and drying could even been undertaken during the night, when power is both cheaper and often at a surplus.

Processing

Slow pyrolysis is a technique designed to drive towards maximum char production, by slowly heating biomass in the absence of oxygen to a moderate temperature threshold (<550°C). Dried microalgae biomass that is fed into the pyrolysis reactor is assumed to have a final moisture content of 5% (as received from the spray dryer in the preceding step), in order to calculate the energy requirements to carry out the pyrolysis process. Based on the application of computer aided thermal analysis (CATA), the process energy inputs to pyrolyse *T. chui* to a temperature of 550°C has been calculated as 1.1 MJ/kg of dry biomass (Grierson et al., 2009).

A variation within the processing stage is introduced in this LCA, whereby chemical solvents (MeOH:DCM in a 9:1 ratio) are employed to extract the natural lipid fraction from the *T. chui* biomass, prior to slow pyrolysis of the residue. This is based on earlier work that investigated the general viability of this technique, which found that extracting and thereby preserving high value, natural lipids and other compounds (up to 15%/wt from *T. chui* cells) can lead to an increase in total oil yield when combined with slow

pyrolysis processing of the residue (Grierson et al., 2011a). What remains to be explored is how this approach impacts on environmental outcomes across the microalgae life cycle on an industrial scale, given the inherent ecotoxicity and complex recoverability, albeit re-use potential of the chemical solvents.

Products/Use

Fundamental data relating to the thermal and chemical properties of *T. chui* and the intermediary products derived from slow pyrolysis processing data presented in Chapters 3 to 5 were used to populate this LCA model. To simplify the application of the selected impact assessment method, the downstream product variants are based on the following four possible processing and product scenarios, later referred to as such in various tables:

- Slow pyrolysis of dried algae biomass for production of:
    - **Scenario 1:** Electricity
    - **Scenario 2:** Electricity and Biochar (allocation required)

- Direct solvent extraction of lipid from dried algae biomass for production of:
    - **Scenario 3:** Biodiesel and Electricity (allocation required)
    - **Scenario 4:** Biodiesel; Electricity and Biochar (allocation required)

6.3 Results and Discussion

6.3.1 Cultivation impacts

Table 22 summarises the characterised environmental impacts associated with a single ton of microalgae biomass cultivation, based on the 80ha closed PBR model. The greenhouse gas balance of the microalgae biomass cultivation stage (*T. chui*) reveals a net negative result in relation to global warming expressed in CO_2 equivalent, despite the energy intensity associated with pumping water, suspending culture, maintaining inflation of the PBRs and delivering flue gas to the culture.

Table 22. Characterisation of environmental impacts from cultivation of microalgae biomass, in dry weight equivalent (per ton)

Impact category	Unit	Microalgae	Soybean	Canola seed
Global Warming	kg CO2 eq	-222	243.3	738.5
Eutrophication	kg PO4 eq	1.1	0.15	0.42
Land use	Ha a	0.001	0.5	0.8
Water Use	kL H2O	96.2	0.6	2.8
Human toxicity, cancer	CTUh	2.0 x10-9	1.2 x10-9	2.9 x10-9
Human toxicity, non-cancer	CTUh	2.0 x10-10	2.0 x10-10	4.6 x10-10
Ecotoxicity	CTUe	0.07	0.01	0.05
Acidification	kg SO2 eq	24.9	1.4	5.4
Photochemical Smog	kg NMVOC eq	9.8	1.3	3.4
Non-renewable Fuel Depl.	kg oil eq	605.4	62.2	174.9
Mineral Depletion	kg Fe eq	827.3	28.1	155.5
Respiratory effects	kg PM2.5 eq	3.1	0.24	0.87
Ecopoints (total)	**p**	**2.23**	**0.67**	**1.59**
Equivalence in Ecopoints	**p/GJ**	**0.138**	**0.039**	**0.056**

Effectively, for every ton of microalgae biomass grown adjacent to a power station using this cultivation system, there is a net reduction of 220 kg of carbon dioxide equivalent removed from the atmosphere, driven by photosynthesis. Given the biochar component of this study and the biological carbon capture and sequestration opportunity (bio-CCS) that this potentially represents, it is important to account for an initial biological capture

component (tabled as a negative). This is so that any allowance made for carbon later stabilised and thereby ‘sequestered’ in soil through the application of biochar will effectively remain therein, from an LCA accounting perspective.

Additional indicators of note in this cultivation model include water use, wherein 96.2 kL of water is required per ton of (DW) algae biomass cultivated. Evaporation from the PBRs for which fresh ‘make-up’ water is required to stabilise salinity is directly attributable to the majority of this measured impact per ton (88.8 kL), with 4.4 kL being associated with fertiliser production. Other indicators linked to power generation and fossil energy use, such as acidification (kg SO_2 eq), photochemical smog (kg NMVOC eq) and non-renewable fuel depletion (kg oil eq), register as 24.9, 9.8 and 605.4, respectively, per ton of DW product. The high readings associated with these metrics reflect the electrical intensity of the algal cultivation process itself, when compared with conventional farming techniques, in addition to reflecting the inputs associated with fertiliser production. Despite being included in the method, neither ozone depletion (kg CFC-11 eq), or ionising radiation (kg U235 eq) registered at all, hence are omitted entirely from Table 22.

6.3.2 Cultivation to processing gate

Figure 29 presents a ‘stacked column’ view of microalgae cultivation and harvesting combined together (incorporating primary, secondary and tertiary dewatering, and the spray drying stage), broken down by impact category and normalised into Ecopoints (p). Leading on from Table 22, the biological capture of carbon dioxide from flue gas contributes a net weighted reduction in global warming impact during cultivation of -0.17 Ecopoints per ton of biomass cultivated, counteracting the emissions of linked processes such as water recirculation, culture suspension and fertiliser production that brings the balance of all phases to 0.96 p/t. Total aggregated impacts relating to water use (0.64 p/t), acidification (1.45p/t) and photochemical smog (0.7p/t) are also prominent, reflecting energy intensity both in terms of direct (e.g. electricity associated with moving water around and maintaining culture suspension) and indirect (e.g. intensity of fertiliser production) impacts.

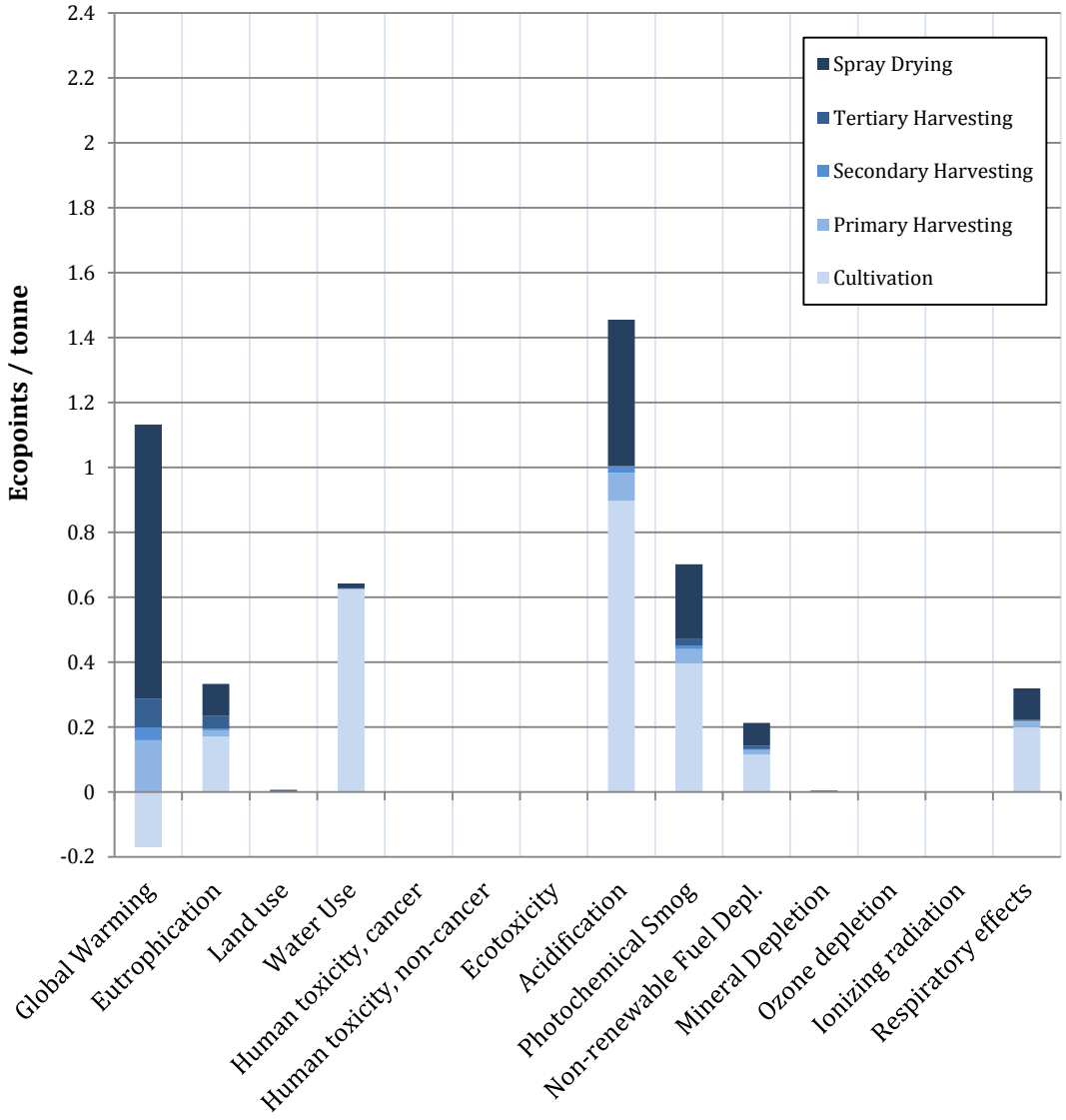

Figure 29. Relative environmental impact contributions per tonne of algae biomass in Ecopoints – cultivation and harvesting stages (p/tonne)

The largest contributing factors linked to acidification during cultivation are the embodied impacts associated with fertiliser production and electricity consumption (flue gas delivery), together representing over 60% of the total Ecopoint score of 1.45 points in this category. This is also reflected in the high non-renewable fuel depletion indicator, made worse by location in a region heavily dependent on coal-fired electricity. Nutrients utilised in the growth cycle of the microalgae have an impact revealed in the eutrophication indicator also (0.17 p/t). The high volume of water use (mostly due to evaporative losses)

represents a significant proportion of overall impact (0.64 p/t) while land use is negligible (<0.01 p/t) since scaled microalgae cultivation will notionally occupy non-arable land unfit for any other application. Mineral depletion does register though likewise equates to an almost negligible impact overall in terms of normalised and weighted Ecopoints per tonne, as do human and eco-toxicity indicator categories.

Only the cultivation stage yields any net benefit in relation to global warming impact, with all other harvesting stages having an impact to varying degrees. Spray drying is a formidable contributor to environmental impact overall and is a major standout in all categories related to electricity use and all impacts associated with it, given the energy intensity of this activity. Throughout an entire year of algae biomass cultivation and harvesting on a 80ha farm, spray drying would notionally represent a contribution of characterised CO_2 eq that is more than 5 times (10,376 tonnes) that of the next most GHG intensive process, namely primary harvesting at 2,240 tonnes (cultivation generates more GHG emissions however this is counteracted by photosynthetic fixation of carbon).

While significant, global warming impact is ultimately less than half of the aggregated environmental impact of the drying stage, demonstrating the importance of broadening assessment scope to consider additional environmental impact categories. Also, the net negative Ecopoint result for cultivation in relation to the global warming indicator masks the fact that the CO_2 harnessed during photosynthesis is strongly countered by the energy intensity directly or indirectly associated with this activity. The impacts of other categories relevant to power generation (observed in Queensland where coal forms a major part of the fuel mix) underscore this, with acidification, photochemical smog, non-renewable resource depletion and respiratory effects (from particulates) represented strongly in the levelled Ecopoint score.

Otherwise, the primary, secondary and tertiary harvesting steps are relatively benign, even when compared with the cultivation stage. The electro-flocculation process (primary harvesting) consumes the most electricity overall and therefore features prominently, though admittedly this process is working with algae in dilute suspension. Centrifuge

operation (tertiary harvesting) appears to be reasonably efficient in this instance when compared with other technologies as it is preceded by two pre-concentration steps that reduce the dewatering load.

The fact that the impact of microalgae biomass cultivation outweighs the primary, secondary and tertiary harvesting steps combined does not necessarily speak to the exceptional efficiency of the latter, rather it highlights by inference just how far scaled, closed cultivation systems need to be innovated in order to achieve an environmentally and (by implication) commercially acceptable outcome. A hierarchy of options would suggest that reducing design and operational complexity is a promising strategy for realising major improvements, before tackling the more difficult prospect of improving biomass productivity per unit area, though both must surely be considered.

6.3.3 Comparison with alternative feedstocks

A comparison between producing 1t of microalgae biomass (dry weight equivalent, in suspension) with standing crops of soybean (Soybean/AU U from the Australian Unit Process LCI) or canola seed (Canola Seed, at farm/AU U from the Australian Unit Process LCI) is also made in Table 22 (2007a). As potential biofuel feedstocks, each represents a ‘cultivation-to-harvesting gate’ scenario only. The data suggests that despite inefficiencies in the modelled PBR design, the overall environmental impact of the microalgae biomass cultivation step is quite comparable. Global warming metrics aside, mineral depletion associated with microalgae cultivation, relative to soy and canola production is extremely high, though this has little impression in the weighted impact of cultivation.

Process energy intensity is clearly a major factor in relation to the microalgae cultivation system proposed in this work. However, a decision to avoid reporting cumulative energy demand here is reflective of that fact that this offers only a narrow perspective that fails to tell the entire story of environmental impact. Comparative water consumption is also high for microalgae and gives cause for concern, though this is again somewhat ‘hidden’ in the final Ecopoint result. Clearly a major benefit of microalgae in the ‘food versus fuel’

sense, is the lack of impact related to occupation of arable land, which makes almost no contribution to the final Ecopoint comparison. A final levelled comparison made in Ecopoints (p) on an equivalent energy (GJ) basis, places microalgae biomass cultivation in this study approximately 3.5 times the impact of soybean and just under 2.5 times that of canola seed. Based on the open pond cultivation system modelled by Campbell et. al. (Campbell et al., 2011) this Ecopoint figure would be around 50% of soybean, thereby highlighting the inherent operating intensity of closed culturing systems operated at scale.

6.3.4 Comparison with benchmark indicators

Comparison of the overall impact of the various microalgae processing scenarios in relation to output products (that incorporate downstream processing and product use stages) is presented in Table 23. The results for electricity production per MWh suggest that the route by which a natural lipid product is extracted from microalgae for biodiesel production in the first instance, prior to pyrolysis of the residue for generation of electricity and/or biochar, could lead to a better environmental outcome than where the raw biomass is pyrolysed outright. This is because the total amount of electricity produced in scenario 3 and 4 is reduced, relative to biodiesel and biochar that inherit a greater share of the overall impact. Sensitivity to the low value of electricity relative to biodiesel is potentially also a contributing factor in this instance however this is important to view in the commercial context in which such a process would operate, and therefore, the degree to which environmental impact would be economically allocated.

In all scenarios presented in Table 23, the global warming impact per MWh for electricity generated from microalgae pyrolysis co-products is around 40% or less of the benchmark indicator, being the Queensland electricity grid (0.94t CO_2/MWh). Even where the pyrolysis co-products are used in Scenario 1 purely for the generation of electricity, there is still a reduction of two-thirds in the CO_2 eq emitted for every MWh produced. This is encouraging on one level but still represents a net production of GHG to achieve this outcome. The total Ecopoint score is approximately the same as the Queensland benchmark (1.6 p/MWh) in relation to Scenarios 1 and 2, reflecting again

the considerable aggregated impact of other environmental indicators associated mostly with cultivation (nutrients, flue gas delivery and water) and drying.

Table 23. Relative environmental impact of downstream products based on four scenarios

End Product: Electricity	**tCO2 eq/ MWh**	**Ecopoints/ MWh**
Scenario 1: Pyrolysis - electricity	0.33	1.5
Scenario 2: Pyrolysis - electricity + biochar	0.38	1.7
Scenario 3: Oil extraction; residue pyrolysis - electricity + biodiesel	0.2	0.8
Scenario 4: Oil extraction; residue pyrolysis - electricity, biodiesel + biochar	0.23	0.8
Queensland Electricity Grid	***0.94***	***1.6***
End Product: Biochar (for soil amendment/bio-CCS)	**tCO2 eq/ tonne**	**Ecopoints/ tonne**
Scenario 2: Pyrolysis - electricity + biochar	0.66	2.9
Scenario 4: Oil extraction; residue pyrolysis - electricity, biodiesel + biochar	0.40	1.4
Fertiliser NPKS	***1.14***	***4.0***
End Product: Biodiesel	**tCO2 eq/ GJ**	**Ecopoints/ GJ**
Scenario 3: Oil extraction; Residue pyrolysis - electricity + biodiesel	0.32	1.1
Scenario 4: Oil extraction; residue pyrolysis - electricity, biodiesel + biochar	0.32	1.1
Soy Biodiesel	***0.12***	***0.3***

6.3.5 Prospects for bio-CCS

A focus on biochar reveals that between 0.4t – 0.66t of CO_2 eq is attributable to the production of 1 t of biochar, depending on the scenario. This result indicates that pyrolysis of microalgae biomass for a bio-CCS outcome based on the modelled value chain is not yet within reach of achieving a net reduction in global warming impact, even when taking biologically sequestered C into account through application of biochar to soil. This result includes the non-labile C measured at 60 wt/% of *T. chui* biochar (Chapter 5 and Grierson et. al., 2011b) and means that around half a tonne of CO_2 eq must be emitted to permanently sequester 90 kg of carbon with this value chain established. That said, while the boundaries of this attributional LCA analysis do not extend to assessing the impact of biochar application itself, it has been reported that in an agronomic context biochar can deliver an abatement benefit in the order of 2.6-16 tCO_2 eq/t once applied hence these embodied impact results could be significantly more optimistic when a different system boundary is applied (Gaunt & Cowie, 2009).

A discussion of the net impacts of biochar production through slow pyrolysis of biomass feedstocks, in this case stover, yard waste and switchgrass, provides a sobering contrast (Roberts et al., 2009). All of these delivered a net benefit, both in terms of energy produced as well as reductions in GHG emissions. As effective models of waste utilisation, what is lost in each of these instances in relation to land use changes is more than made up for by the lack of cultivation impacts and processing intensity. In this work, the conclusion is drawn that the selection of pyrolysis feedstock is paramount in relation to avoiding “unintended consequences such as net GHG emissions or consuming more energy than is generated, and also to ensure economic and environmental sustainability throughout the process life cycle” (Roberts et al., 2009).

It is tempting to conclude that the inherent energy intensity of culturing, dewatering and drying microalgae biomass in preparation for pyrolysis renders this entire pathway unattractive from an environmental perspective, at least in relation to the existing system design. Commercially, the process and energy intensity, along with capital and operating expenditure are also likely to make pyrolysis a challenging conversion pathway to realise

for microalgae, when compared with alternative options. It should be highlighted here that this entire study is set in Queensland, one of the most pollution intensive electricity grids in Australia with a predominance of black coal in the generation mix. This has flow on effects throughout the model and presents what can in some respects be considered an unflattering picture. That is, the results of this study are by default modelled based on 'business as usual' whereby all unit processes are dependent on regional electricity provision sourced directly from the grid and in Queensland, this is reasonably carbon intensive.

6.3.6 Process innovation

Realistic opportunities for reduction of the overall impact of the microalgae pyrolysis value chain are clearly apparent from the results presented in this work, though much of this is generically applicable to algae systems in general. Commencing with the cultivation stage, there is significant opportunity to access electricity from either lower emissions sources via the grid and/or by integrating renewable energy into the operation. Solar pumps for moving water around and solar PV direct drive motors for microalgae suspension could easily be integrated to provide significant reductions in operational energy. Leveraging wastewater or even nutrient found in animal wastes is another obvious way to alleviate the embodied impact of cultivation to substitute conventional, industrial fertiliser. Accounting for reductions in environmental impact through the service of bioremediation delivered during algae cultivation in relation to heavy metal contaminants in ash dams for instance, is one co-product that improves this picture also.

Since pressurising and delivering flue gas to the algae culture is inherently energy intensive and problematic under any cultivation regime, it may be possible to use a hypersaturation system to 'pre-load' carbon into the growth medium at a centralised point (much as a Speece cone already does), next to the point of flue gas desulphurization, which then negates the need for an extensive flue gas distribution network. All of these innovations have potential to deliver reductions across multiple categories of environmental impact.

While a spray dryer is a proven technical solution for industrial food manufacturing, its use for a bio-CCS oriented outcome at scale may not be viable and could perhaps only be justified on economic grounds, where a high value product pathway is pursued, such as in relation to nutriceuticals (van Beilen, 2010). In the context of pyrolysis, there is no way to avoid the requirement to deliver a dry product for thermal decomposition and the intrinsic enthalpy of vapourisation of water remains. As such, the considerable impact of spray drying may be further reduced by integrating concentrating solar thermal technology or even entirely replacing this method with a passive solar or waste heat driven kiln operating at lower temperatures and with much longer residence times.

6.3.7 Sensitivity analysis

Four sensitivity prospects have been considered, including where various process innovations suggested in the previous section take effect (Table 24 – A - D). Where average productivity of the microalgae culture (A) is reduced by 50% with no other changes made to the system, then the life cycle footprint will obviously become more intensive. That is, for the same 80 ha area of production, the same amount of evaporated water and operational energy requirements is being incurred during all stages of production (even though half as much microalgae biomass is being produced). Reductions in nutrient and CO_2 demand, as well as processing inputs (e.g. methanol used in transesterification and solvents used in oil extraction) will fall however so there is a decrease in the relative impact from these items.

In this example, the intensity of CO_2 eq emitted per tonne of algae cultivated becomes a net burden, shifting from -222 kg CO_2 eq/t reduced, to 565 kg CO_2 eq/t. Overall however, the embodied environmental impact per tonne of product in some instances only shows a relatively minor increase. In relation to Scenario 3 for instance (wherein both biodiesel and electricity are being produced), as a measure of impact per MWh electricity produced, the Ecopoint score per MWh increases by only 12.5% (from 0.8 to 0.9 p/t) even as global warming impact rises by 50%. This is a reflection of the overall proportional reduction in process intensity from flue gas delivery and nutrient supply, both of which are clearly pivotal items in terms of impact (this phenomenon is observed in all scenarios, in relation to all products).

Another obvious sensitivity analysis was conducted in relation to pricing of biochar in particular (Table 24 - B), since this is an item with high potential to distort or change results dramatically in an econconomic allocation scenario, assuming that a mature market becomes established. A five-fold increase in biochar price to $250/t clearly increases impacts in relation to the production of biochar itself, with a multiplier in the range of approximately 3-4 times, though this is again somewhat overshadowed by the high price of liquid fuels. As previously outlined, no known LCIA method in Australia currently incorporates any soil salinization indicator, hence this impact is currently unknown and effectively, unreported at present. As *T. chui* is a marine microalga and its biochar product is likely to be highly sodic, this impact is an important consideration before drawing any conclusions as to the suitability of the material for this application (Grierson et al., 2011b).

Interestingly, even a dramatic increase in the price of biochar does little to impact on either GHG emissions or Ecopoint impact in relation to biodiesel, which is largely unaffected given its relatively high cost. Electricity production is a mixed outcome when the value of biochar is increased, with both indicators falling by around 50% in relation to Scenarios 1 and 2, and little change in relation to Scenarios 3 and 4. This is again likely to be due to the distorting impact of the value of biodiesel as well as its added process intensity, relative to other products.

Taking into account possible design innovations, Table 24 – C considers the instance whereby an effective 75% reduction in industrial fertiliser can be achieved through substitution with animal waste and/or wastewater sources, in addition to the prospect of using solar energy to drive the suspension sled and PBR inflation fan during daylight hours (75% reduction in grid energy impacts). The outcome of these measures is considerable, with the global warming and Ecopoint impact for all non-biodiesel scenarios falling by as much as 50%. Since nutrient input based on conventional industrial manufacture of fertiliser represents a considerable proportion of microalgae cultivation impacts, this lends weight to the argument that utilisation of wastewater streams is indeed important to delivering a positive outcome (Park et al., 2011; Pittman et al., 2011). Municipal wastewater treatment facilities, agriculture and aquaculture farms

Table 24. Environmental impact of downstream products based on four sensitivity scenarios, relative to the base configuration

Sensitivity Test	**A**		**B**		**C**		**D**	
End Product: Electricity	**tCO2 eq/ MWh**	**Ecopoints/ MWh**	**tCO2 eq/ MWh**	**Ecopoints/ MWh**	**tCO2 eq/ MWh**	**Ecopoints/ MWh**	**tCO2 eq/ MWh**	**Ecopoints/ MWh**
Scenario 1	0.53	2.0	0.20	0.9	0.18	1.2	-0.02	0.9
Scenario 2	0.61	2.2	0.23	1.0	0.21	1.3	-0.02	0.9
Scenario 3	0.3	0.9	0.2	0.8	0.2	0.6	0.1	0.5
Scenario 4	0.31	1.0	0.19	0.7	0.17	0.7	0.1	0.6
End Product: Biochar (for soil amendment)	**tCO2 eq/ tonne**	**Ecopoints/ tonne**	**tCO2 eq/ tonne**	**Ecopoints/ tonne**	**tCO2 eq/ tonne**	**Ecopoints/ tonne**	**tCO2 eq/ tonne**	**Ecopoints/ tonne**
Scenario 2	1.05	3.8	1.95	8.7	0.35	2.3	-0.03	1.6
Scenario 4	0.53	1.7	1.66	5.9	0.29	1.2	0.17	1.0
End Product: Biodiesel	**tCO2 eq/ GJ**	**Ecopoints/ GJ**	**tCO2 eq/ GJ**	**Ecopoints/ GJ**	**tCO2 eq/ GJ**	**Ecopoints/ GJ**	**tCO2 eq/ GJ**	**Ecopoints/ GJ**
Scenario 3	0.43	1.3	0.32	1.1	0.24	0.9	0.13	0.7
Scenario 4	0.42	1.4	0.27	0.9	0.24	1.0	0.13	0.8

Legend: Scenario 1 = electricity only; Scenario 2 = electricity & biochar; Scenario 3 = biodiesel and electricity; Scenario 4 = biodiesel, electricity and biochar. A = -50% reduction in culture productivity; B = increase in the price of biochar to $250/t; C = Substitution of 75% (waste) nutrients & 75% renewable energy integration into PBR suspension and inflation; D = Substitution of 75% (waste) nutrients & 75% renewable energy integration into PBR suspension and inflation, combined with 50% efficiency reductions in gas delivery and spray drying.

all present possible sources of nutrient that could be employed for the reduction of this burden, representing an 'industrial ecology' strategy that also offers commercial and environmental benefits (Grönlund et al., 2004; Sturm & Lamer, 2011).

Finally, Table 24 – D presents a circumstance in which the exact same process efficiencies and reduction feature as in Table 24 – C, with the additional prospect of the energy involved in CO_2 diffusion and gas distribution being cut by 50% by centralising in a hypersaturation facility located near the source of flue gas. Added to this is a further 50% (hypothetical) reduction in drying energy based on the existing load requirement (effectively, 15% of the total spray drying evaporative load at present), to be achieved either by improving energy recovery or using an entirely new, more efficient (likely passive solar) drying method. Results indicate that with the combination of these innovations, we would see the global warming indicators for electricity (Scenarios 1 & 2) and biochar (Scenario 2) trending negative to a point at which a small net carbon reduction could theoretically be achieved.

6.4 Conclusion

The ability for microalgae-based products to compete effectively at scale in new and existing markets will inevitably be based on price, but increasingly also in terms of demonstrating comparable reductions in environmental impact (relative to incumbent products). The sheer volume of many of the process inputs necessary to achieve any meaningful scale of microalgae biomass production in a closed culture environment, namely in terms of water, CO_2, nutrient, non-productive land and process energy, requires a sustainable approach.

Aggregate impacts of various pyrolysis co-product pathways that consider electricity, biochar and biodiesel production, based on the tonnage of *T. chui* microalgae biomass cultivated annually on an 80ha farm, indicate that the lowest impact scenarios are where the natural lipid fraction is extracted first for biodiesel production, and then the residue pyrolysed for electricity production as in Scenario 3, with biochar otherwise routed to soil amendment in Scenario 4. Notably, a simple economic evaluation indicates that the value of the respective revenue streams for each scenario based on prevailing

economics is such that the biodiesel production pathways (Scenarios 3 & 4) are likely to yield more than double the income of the pyrolysis of raw biomass processing routes (Scenarios 1 & 2).

Application of the adapted LCA method highlights that the case for bio-CCS via microalgae-derived biochar is not currently persuasive, given the material and energy intensity of the overall value chain. Without considerable innovation, the credible marketing of a microalgae-derived biochar product based on environmental virtue would have to emphasise the holistic benefits of returning carbon to soil, including demonstrating the multiplying benefits that this can enable in agricultural systems, instead of focusing on direct greenhouse gas abatement potential alone. Process nutrients in the form of fertiliser and energy required to dry microalgae biomass for pyrolysis are also major challenges to overcome, although utilisation of nutrient-rich wastewater and process heat from symbiotic industries could change this picture quite dramatically.

In the case of LCA of microalgal biomass, economic allocation is a key methodological issue that needs to be strictly consistent in relation to assessment of all technologies and pathways, as this enables more balanced decision making to be made based on both utilisation of wastes and generation of co-products. From a LCA perspective, the issue of allocating environmental burden becomes a fulcrum on which microalgae systems could ultimately be portrayed as either a profound, systemic alleviator of many of our macro-environmental challenges (such as climate change or eutrophication), or else justification to proceed no further with this biomass solution given its embodied impact.

The overall environmental impact of the microalgae biomass (*T. chui*) and pyrolysis processing regime presented demonstrates high energy intensity associated with cultivating and achieving a suitably dry feedstock that can be pyrolysed. As such, microalgae biomass as a feedstock for large scale bio-CCS through application of biochar will require considerable advances in cultivation technology, harness of waste nutrients from aligned industries and adoption of alternate drying methods. Where a biofuel product is desired, processing technologies such as hydrothermal liquefaction

(HTL), that can process algae biomass *in situ* where it is less than 20% in solids concentration may be more attractive, requiring less dewatering energy overall (especially drying).

Chapter 7: Conclusion and Recommendations

The aim of this thesis was to test the central premise that it is possible to achieve large scale fossil energy displacement and meaningful volumes of carbon abatement by combining a highly productive form of biomass (in this case microalgae) with slow pyrolysis processing, to produce renewable oil, gas and char. With a specific interest in bio-CCS through the addition of biochar to soil that would contribute to net permanent reductions in atmospheric CO_2 levels, this undertaking was made on the basis of evaluating what may be termed a 'carbon neutral or better' value proposition. A clear 'first principle' on which this system was constructed depended on determining whether or not the aggregate impacts of production would generate less carbon emissions overall than are emitted during product use. Beyond this, additional embodied environmental impacts were also important to consider including those indicators relating to macro issues such as eutrophication, acidification and even human health.

A more complete understanding of microalgae as a biomass feedstock was sought through a program of analytical work intended to elucidate on the fundamental thermochemical characteristics and behaviour of a candidate species, *Tetraselmis chui*, under slow pyrolysis conditions. To consider this in greater detail and despite any scaled examples of such a microalgae-to-pyrolysis operation having been constructed to date, an LCA of this theoretical prospect was developed in order to provide insight into the likely consequences of attempting such a scheme and to also highlight specific levers for innovation that would enable this concept to be realised in due course, or to at least close the gap with reality.

Early experimental work revealed a number of insights that both reinforce and extend the existing body of knowledge in this area. Specific results of the biochar prospect in this study suggest that it may be possible to achieve a net reduction in carbon over the life cycle of the process, however this will require considerable improvements in cultivation and dewatering (including drying) technologies to be innovated. Much of the evidence points to open photoautotrophic systems as a preferred cultivation solution for co-location with industrial symbiants, such as power generators, in that these designs tend

to involve far less complexity and by definition, less capital and operating intensity than closed, PBR systems. Undoubtedly, the closed culturing system design considered in this study may have limited advantage in relation to supporting higher culture productivity, along with greater control of system parameters and contaminants, however the likely trade-off with capital and operating intensity is difficult to justify at present.

The microalgae value chain offers considerable opportunity for optimisation, notwithstanding that that there are no farms of industrial scale currently in operation. However, there has been an explosion of research in the general field of algae biomass cultivation and much investment is now entering the sector. In seeking to identify improvements in the life cycle footprint of scaled microalgae production, it should also be acknowledged that microalgae farm systems will inevitably be obliged to extract maximum commercial value out of the biomass resource that they grow. As such, at current (low) prices for energy, there will always be a tension between 'highest value' versus 'greatest good' and this will influence end product use and therefore processing choices. In particular, until biochar matures as a legitimate abatement product and accrues demonstrable market value, it may be subject to substitution pressure.

From a sustainability perspective, the overriding concern is that a scaled microalgae biomass and pyrolysis processing regime, in a bid to address many of the legitimate concerns that surround the continuing consumption of fossil fuels, could in fact come to represent an unwitting lurch of human society from one fundamentally unsustainable paradigm, into another. While there is no inference that such a scheme would in any way come to supplant fossil resource consumption in its entirety, there are several reasons why even at modest scale – as an abatement 'wedge' (Pacala & Socolow, 2004) - this concept deserves scrutiny.

Firstly, microalgae farms have the potential to occupy large tracts of otherwise unusable land for any conventional form of agriculture. This makes them a useful application for cheap and abundant landholdings that do not come into direct competition with food production and thereby sidestep many of the negative issues that plague the biomass industry. For countries such as Australia, with large tracts of flat, degraded land,

proximate access to an extensive coastline (for access to seawater as growth medium) and high rates of solar insolation, many of the key criteria for microalgae cultivation would seem to be in place, though access to point sources of CO_2 is a notable limiting factor (Campbell et al., 2009). In any case, there may be little to hold back the march of an industry that promises a renewable source of liquid transport fuel and/or baseload electricity-capable biomass resource, where it provides security of supply, reduced sovereign risk and 'drop in' capability to existing hydrocarbon infrastructure.

Secondly, the increasing motivation of concentrated, point-source greenhouse gas emitters, such as power generators and heavy industry, to abate carbon and thereby avoid punitive taxes and raise their environmental credentials, has added some significant momentum to this endeavour. Microalgae have now been shown to be capable of capturing carbon directly from the flue stacks of such facilities, many of which have few technically viable and affordable means of achieving emissions reductions. In the end, the choice for such facilities in this scenario is closure and the accrual of valuable stranded assets, or, the adoption of a scalable, affordable abatement solution using algae biomass – suffice it to say that there are multiple levels of motivation here.

Third, the growth of vast quantities of aquatic plant biomass demands equally vast quantities of nutrient in order to be a success, as with any intensive farming operation. Conventional synthetic fertilisers and pesticides represent a considerable imposte on the environment, both directly and indirectly, and suggest that if meaningful displacement of fossil resources where to occur, this would require a commensurately large application of such that would potentially enact a heavy environmental burden.

Finally, the issue of fresh water scarcity is prevalent given that on a microalgae farm, cultivating either a fresh or marine species demands large volumes of water to be used as growth medium and/or make-up water for the control of salinity. Given the inherent intensity of modern water treatment facilities that provide reticulated supply or indeed the strain on ecological systems where either ground or surface water of natural origin is utilised, the scaled, albeit localised demand in this regard provides further pause,

notwithstanding the considerable energetic costs of moving water around in large volumes.

Although there is now considerable interest and investment in algal research happening around the world today with the goal of delivering high volume carbon abatement and biofuel/bioenergy production in mind, no projects have yet achieved any significant size and hence are yet to present any serious environmental threat or set a precedent in this regard. In addition to the challenges of engineering such a farm, the dearth of commercial microalgae projects for anything other than high value products is as much a function of process economics as anything else and this will continue to constrain industrial development towards service of bioenergy and biofuels markets. The ability to cultivate microalgae at scale is simultaneously connected to issues of obtaining a social and environmental 'license to operate', as well as achieving reductions in capital and operating intensity through bioengineering innovation. Ultimately, leveraging energy, material and overall process efficiencies will be the only means for this fledgling industry to develop beyond the laboratory or delivery to niche bioproducts markets.

Utilising LCA techniques to guide the innovation process can help to ensure that efforts and investments are being directed to the areas of greatest impact (and thereby cost and risk) reduction, in order to deliver scale. Large-scale cultivation and harvesting of microalgae is difficult enough, as successfully sustaining culture and then achieving any degree of separation of microscopic plant cells from the growth medium is by definition a system made up of many unit processes. In order to improve the life cycle profile of microalgae biomass, a focus must first be placed on innovating the process of cultivation to maximise carbon capture at the lowest possible cost and embodied impact. However, these initiatives are valid regardless of the downstream processing technology to be employed or the product outcome that is sought and will depend upon prevailing market demand for various products, including carbon abatement.

The value chain that is enabled via pyrolysis of microalgae biomass represents an inherently complex picture to assess from an LCA perspective as there are multiple applications that can potentially be pursued once the by-products have been delivered.

Importantly, and with a view to slow pyrolysis in particular, the production of biochar provides the only known means to achieve long-term storage of carbon in soil. Any other utilisation of biomass resources by definition achieves only a ‘carbon offset’ as opposed to permanent storage or ‘sequestration’ since the carbon that is captured during photosynthesis will typically be released back into the carbon cycle within a 100-year timeframe generally regarded as meaningful for trading purposes by governance and regulatory bodies such as the IPCC.

However, therein lies a dilemma. Coupled with the imperative to deliver a dry feedstock to the pyrolysis ‘processing gate’, this scenario is especially sensitive to questions of process efficiency since microalgae are a water-borne resource growing in highly dilute suspension. In this case, drying (following pre-concentration and dewatering) needs to occur to the maximum conceivable commercial threshold of <5% in order to deliver a biochar product outcome via pyrolysis, in addition to the co-products of bio-oil and biogas, and hence the energy requirement for supporting this outcome is a profound factor that cannot be overstated.

As such, the measure of whether or not slow pyrolysis of microalgae can deliver meaningful carbon abatement through bio-CCS becomes as much a question of what is the best economic and environmental choice for utilisation of this biomass resource, from the ‘processing gate’ onwards, as opposed to whether or not bio-CCS is possible. With this in mind, extraction of high value lipid from microalgae as an intermediary processing measure is likely to be both responsible and advantageous. While biodiesel through transesterification was a product considered in Chapters 5 and 6, specialty chemicals and other petro-chemical feedstock substitutes through direct extraction are worthwhile to consider also prior to pyrolysis of the residue, as increasing temperature otherwise quickly denatures the natural lipid fraction.

Nevertheless, findings from this work are that unless the drying step that enables pyrolysis can take place with little or no energetic burden through the leverage of waste heat and/or passive solar resources, then it is likely that the incremental difference in embodied environmental impact relative to other potential processing pathways or

product routes will be counter-productive to achieving greenhouse gas and other environmental impact reductions. That is, there is a real risk that dewatering (drying) to 5% or less moisture will likely exceed any carbon reductions that might otherwise occur through the application of biochar to soil – without careful consideration, the benefits are likely to outweigh the costs.

The experimental results derived in this study provide the parameters within which this would need to operate successfully from a bio-CCS standpoint. One must assume that the cultivation process will need to be innovated to ensure that the delivery of 1t of biomass grown in dilute suspension, through industrial symbiosis with an intensive CO_2 emitter, can be achieved at a considerable net carbon draw-down and with limited environmental impact. From this point, if (in the order of) 9% of the carbon fixed in microalgae biomass is assumed as the long-term stabilisation quotient to be delivered through biochar application, then the final drying stage that enables pyrolysis (including the 1100MJ/t of energy required to drive this process) would have to incur a total process burden of less than 330kgCO_2eq/t in order to offer any net benefit in terms of global warming impact, relative to other processing pathways. Since this work has demonstrated that the process energy offset provided by combustible biogas that evolves during decomposition exceeds the energetic requirements for pyrolysis, it can be argued that the pyrolysis process itself can be viewed as self-sustaining. Therefore, it is not pyrolysis processing *per se* that is the issue here rather the pre-conditions required to enable successful thermal decomposition and delivery of viable co-products (i.e. achieving a dry product).

7.1 Recommendations

Recommendations for further study include understanding the environmental benefit of delivering microalgae biomass in industrial symbiosis where bioremediation of water bodies is delivered. That is, where waste nutrients (N, P or K) or even heavy metal contaminants are taken up during cultivation, some consideration of the environmental value of this as it translates into LCA results needs to also be taken into account, including in relation to the specific nutrient offset capacity of biochar. In terms of downstream product use, detailed analysis of the upgrade and/or combustion of pyrolysis

by-products needs to be undertaken to obtain more precise emissions and LCI data for the use phase in order to understand how these products will perform. Furthermore, greater analysis of the value-adding potential of algae biochar application in particular could offer a multiplying effect of greenhouse gas reductions and other benefits that should be quantified. Where marine species of algae are implicated, it is important to also address the issue of soil salinization to qualify the likely impact of broad scale biochar application. Finally, a lack of consistency and comparability makes it difficult to benchmark different microalgae LCA studies and processes effectively. A key recommendation is that the Australian algae biomass industry would be well advised to decide on a standardised approach to LCA that can eventually articulate into consumer product markets, wherein eco-labelling is increasingly becoming a feature. This needs to be based on a common method that enables multiple co-products, both energy-related or otherwise, to be evaluated based on a 'level playing field' LCA approach that enables transparent comparison across all parts of the value chain.

Two other scenarios are important to consider as the microalgae biomass-to-pyrolysis route (with a view to ensuring environmental net benefit) needs to be measured against alternative uses, species and/or processing pathways for utilisation of aquatic biomass. Firstly, given the inherent complexity, infrastructure and operating profile of a microalgae biomass system operating at scale, it is worthwhile investigating macroalgae cultivation for the same application, since harvesting and dewatering is likely to be cheaper, simpler and by definition, of lesser environmental impact and intensity. Secondly, the ability to process biomass in aqueous suspension suggests that supercritical water (SCW) conversion is a competing processing technology that may offer greater environmental benefit in that a substantially reduced dewatering load and elimination of the drying requirement altogether in this scenario reduces the energy inputs and complexities across the overall production system (Xu et al., 2011a).

The conclusion of this study is that it may be possible to achieve a 'carbon neutral or better' outcome through the high volume, slow pyrolysis of microalgae biomass that maximises the production of biochar. However, in order for this to be sustainable both environmentally and economically, innovation across all stages of the cultivation,

harvesting, processing and end-use phases is necessary. In most instances, this equates to necessary reductions in greenhouse gas intensity and environmental impact for various sub-unit processes of 75% or more. Special emphasis needs to be given to the utilisation of waste CO_2, nutrient, water and moderate-grade process heat that it would be necessary to employ though this by default limits the number of production sites available in Australia. Integration of renewable energy will also be important to reduce operational costs and environmental burden, as will identifying a more energy efficient means to deliver scrubbed flue gas to the cultivation system. These measures combined can be expected to pay environmental and commercial dividends over a project design life of 25 years or more.

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Appendix A: Declaration of authorship contributions

Journal Papers

Thermal Characterisation of Microalgae under Slow Pyrolysis Conditions

Contributions to the paper were as follows:

(87.5%) Scott Grierson assisted in the cultivation of microalgae species at Port Stephens, with the supervision and assistance of Ross McGregor. Scott then undertook the thermal conversion and analytical work in the laboratory at Macquarie University and managed any outsourced analysis that was necessary. Scott was the primary author and correspondent for the manuscript.
(5%) Vladimir Strezov acted in his capacity as Primary Supervisor in supporting the analytical work and was a major reviewer of the manuscript.
(2.5%) Joe Herbertson supported this work as the industrial sponsor that produced the microalgae samples and provided limited review of the manuscript.
(2.5%) Gary Ellem supported this work as an agent of the industrial sponsor and brokered the partnership that led to cultivation of the microalgae species at the Department of Primary Industries, Port Stephens, also providing limited review of the manuscript.
(2.5%) Ross McGregor acted as the research assistant with the primary responsibility of cultivating and drying the microalgae samples in preparation for analysis, and provided limited review of the manuscript.

Properties of oil and char derived from slow pyrolysis of *Tetraselmis chui*

Contributions to the paper were as follows:

(90%) Scott Grierson undertook the thermal conversion and analytical work in the laboratory at Macquarie University and managed any outsourced analysis that was necessary. Scott was the primary author and correspondent for the manuscript.
(5%) Vladimir Strezov acted in his capacity as Primary Supervisor in supporting the analytical work and was a major reviewer of the manuscript.
(5%) Pushan Shah acted in his capacity as a Post-Doctoral Researcher in supporting the GC-MS and FT-IR work and was a limited reviewer of the manuscript.

Assessment of bio-oil extraction from *Tetraselmis chui* microalgae comparing supercritical CO_2, solvent extraction and thermal processing

Contributions to the paper were as follows:

(85%) Scott Grierson undertook the thermal conversion and analytical work in the laboratory at Macquarie University, as well as SCF extractions at UNSW and managed any outsourced analysis that was necessary. Scott was the primary author of the manuscript.
(5%) Vladimir Strezov acted in his capacity as Primary Supervisor in supporting the thermal conversion work, was a major reviewer of the manuscript and acted as the correspondent for this work (Scott was overseas following submission).
(5%) Sargent Bray acted in his capacity as a Post-Doctoral Researcher in supporting the GC-MS work and was a major reviewer of the manuscript.
(2.5%) Raffaella Mummacari acted in her capacity as the Post-Doctoral Supervisor by providing input into the experimental methods and facilitating access to the UNSW laboratory.
(2.5%) Luu Thai Danh acted in his capacity as a Research Assistant by providing assistance in operation of the SCF extraction system at UNSW.

(2.5%) Peter Foster acted in his capacity as Head of the Supercritical Fluids Group at UNSW and supervised the work.

Life cycle assessment of a microalgae biomass cultivation, bio-oil extraction and pyrolysis processing regime

Contributions to the paper were as follows:

(85%) Scott Grierson undertook the modelling and data collection for this study and was the primary author and correspondent of the manuscript.
(5%) Vladimir Strezov acted in his capacity as Primary Supervisor in supporting the analytical work and was a reviewer of the manuscript.
(10%) Jonas Bengtsson provided input as a recognised industry expert in the field of LCA by assisting with refinements to the model and was a major reviewer of the manuscript.

Conference Papers

Microalgae as an Aquatic Biomass Alternative for Sustainable Energy and Materials Production

(90%) Scott Grierson undertook the modelling and data collection for this study and was the primary author of the manuscript.
(5%) Gary Ellem was a major reviewer of the manuscript.
(5%) Vladimir Strezov was a major reviewer of the manuscript.

Life Cycle Assessment of the Microalgae Biofuel Value Chain: A critical review of existing studies

(95%) Scott Grierson undertook the literature search and review for this work and was the primary author of the manuscript.

(5%) Vladimir Strezov was a major reviewer of the manuscript.

Conference Presentations

Biomass Production in the Context of Climate Change: The Role of Algae in Sustainable Biomass Supply

(95%) Scott Grierson was solely responsible for compiling and presenting this work.
(2.5%) Joe Herbertson provided limited review and input into presentation content.
(2.5%) Vladimir Strezov provided limited review and input into presentation content.

Thermal decomposition, characteristics and behaviour of microalgae during slow pyrolysis

(97.5%) Scott Grierson was solely responsible for compiling and presenting this work.
(2.5%) Vladimir Strezov provided limited review and input into presentation content.

Conference Posters

Life Cycle Assessment of Microalgae Lipid Extraction Techniques

(97.5%) Scott Grierson was solely responsible for undertaking the background modeling, in addition to producing and presenting this poster.
(2.5%) Vladimir Strezov provided limited review and input into the poster content.

Appendix B: Supplementary Information

The following represents supplementary information relevant to Chapter 6.

B1. Input/Output Tables (by Life Cycle Stage)

*Please note in the tables below that ‘Data Quality’ relates to the following hierarchy of data sources (in order of preference) as per manuscript:

1. Published experimental data relating to the thermal and chemical properties of *T. chui* microalgae
2. Unpublished field data provided by industry collaborators
3. Published LCI/LCA studies relating to microalgae systems and products
4. AusLCI datasets provided with SimaPro v7.3
5. The Australasian LCA database provided with SimaPro v7.3
6. International data from the Ecoinvent (v2.2) database, adapted to Australian conditions, as required
7. Derivation, estimation or assumption based on best available data or closest match

B2. Cultivation Phase

B2.1 Algae Biomass Cultivation (50m outdoor PBR; 80 Ha farm, 12 months operation)

Name	Amount	Unit	Allocation (if any)	Comment	Data Quality*
Products & Co-products					
Microalgae biomass (*T. chui*)	10792.32	tonnes	-	Harvest density is 1g/L	2
Harvest volume	1079.23	ML	-	Salt water growth medium	2
Inputs – Materials/Fuels					
Water, process, unspecified natural origin/m^3	958.52	ML	-	Make-up water only to account for total daily evaporation from the PBRs + losses from the spray dryer	2
(Land) occupation; arid, non-arable	80	Ha	-		2
CO2 delivery (flue gas)	19749.95	t	-	As per calculation below, flue gas 13% CO_2	2
Service corridor delivery compressor	*6745.2*	*MWh*	-	*Flue gas compression and delivery, post-desulphurization*	2 / 7
Fertiliser NPKS 32/10, at regional store/AU/U	2182.82	t	-		3
LDPE, Low density polyethylene/AU U	54405.12	Kg	-	60.72kg LDPE per 50 PBR; amortised over 5 year life	2
Inputs – Electricity/Heat					
External water supply/ Discharge energy requirements	449.68	MWh	-	Fresh make up water from reticulated supply	2
Plant harvest & recirculation pumping power requirement	3504.00	MWh	-	For harvest volume and recirculation of recovered medium	2
PBR culture suspension method	3924.48	MWh	-	Operating 6hrs/day per PBR	7

PBR inflation	981.12	MWh	-	Fan providing positive pressure, air flow & evaporative cooling effect	2
Emissions to air					
Water vapour	925.61	ML	-	Evaporative losses from PBR	6
Final waste flows					
Waste, unspecified	0.72	t	-	Particulates	2

B3. Harvesting Phase

B3.1 Primary dewatering (electroflocculation)

Name	Amount	Unit	Allocation (if any)	Comment	Data Quality*
Products & Co-products					
Flocculated microalgae biomass in suspension (*T. chui*)	10792.32	tonnes	-	Harvest density is 1g/L; flocculated biomass in suspension only, hence no losses	2
Culture medium	1079.23	ML	-	Nutrient enriched salt water	2
Inputs – Materials/Fuels					
Microalgae biomass (*T. chui*)	10792.32	tonnes	-	Harvest density is 1g/L	2
Harvest volume (water)	1079.23	ML	-	Growth medium with microalgae in suspension	2
Inputs – Electricity/Heat					
Electricity, high voltage, Queensland/AU U	2376.17	MWh	-	Electroflocculation unit operation	2

B3.2 Secondary dewatering (dissolved air floatation)

Name	Amount	Unit	Allocation (if any)	Comment	Data Quality*
Products & Co-products					
Wet microalgae biomass @ 95% water (*T. chui*)	9928.93	tonnes	-	Take-off density is 18.4g/L; concentration factor x 18.4	2
Residual culture medium	539.62	ML	-	Remaining extra- and intracellular water in post-DAF take-off	2
Recirculated microalgae biomass (ex DAF)	863.39	tonnes	-	8% of microalgae biomass not recovered through DAF, recirculated into cultivation system	2
Recycled culture medium (ex DAF)	10252.7	ML	-	Recirculated into cultivation system	2
Inputs – Materials/Fuels					
Flocculated microalgae biomass in suspension (*T. chui*)	10792.32	tonnes	-	Harvest density is 1g/L; flocculated biomass in suspension only	2
Culture medium (salt water)	10.79	ML	-	Nutrient enriched salt water	2
Inputs – Electricity/Heat					
Electricity, high voltage, Queensland/AU U	534.63	MWh	-	DAF unit operation	2

B3.3 Tertiary dewatering (centrifuge)

Name	Amount	Unit	Allocation (if any)	Comment	Data Quality*
Products & Co-products					
Microalgae paste @ 79% water (*T. chui*)	9432.49	tonnes	-	Take-off density is 214.18g/L; concentration factor from DAF x 15.6 = x 286.6 total concentration factor	2
Remaining water	32.91	ML	-	Remaining extra- and intracellular water in centrifuge paste	2

Recirculated microalgae biomass (ex centrifuge)	496.45	tonnes	-	Lost to centrate; 95% separation efficiency; recirculated into cultivation system	2
Culture centrate (ex centrifuge)	506.7	ML	-	Extracellular, nutrient rich water separated by centrifuge; recirculated into cultivation system	2
Inputs – Materials/Fuels					
Wet microalgae biomass @ 95% water (*T. chui*)	9928.93	tonnes	-	Take-off density is 18.4g/L; concentration factor x 18.4	2
Residual culture medium	539.62	ML	-	Remaining extra and intracellular water in post-DAF take-off	2
Inputs – Electricity/Heat					
Electricity, high voltage, Queensland/AU U	539.62	MWh	-	Centrifuge unit operation at 1 kWh/m^3	2

B3.4 Drying (spray dryer)

Name	Amount	Unit	Allocation (if any)	Comment	Data Quality*
Products & Co-products					
Dry microalgae biomass (*T. chui*)	9432.49	tonnes	-	Powdered product	2
Bonded water	1646	kL	-	Inherent moisture @ 5%	2
Inputs – Materials/Fuels					
Microalgae paste @ 79% water (*T. chui*)	9432.49	tonnes	-	Take-off density is 214.18g/L; concentration factor from DAF x 15.6 = x 286.6 total concentration factor	2
Remaining water	32.91	ML	-	Remaining extra- and intracellular water in centrifuge paste	2
Inputs – Electricity/Heat					
Electricity, high voltage, Queensland/AU U	11004.57	MWh	-	Spray dryer @ 4.2GJ/t water; electricy to heat at 100%	3
Emissions to air					
Water vapour	31.27	ML		95% vapourized through spray drying, not recaptured and recirculated to cultivation system; latent heat recovery	2

B4. Processing Phase

B4.1 Scenarios 1 & 2:

Production (Slow pyrolysis of microalgae biomass)

Name	Amount	Unit	Allocation (if any)	Comment	Data Quality*
Products & Co-products					
Microalgae pyrolysis – bio-oil	4848.30	tonnes	84.6%	27.9 MJ/kg	1 / 7
Microalgae pyrolysis – biogas	924.38	tonnes	3.3%	2.9 MJ/kg	1 / 7
Microalgae pyrolysis – biochar	3659.81	tonnes	12.1%	14.5 MJ/kg	1 / 7
Inputs – Materials/Fuels					
Dry microalgae biomass (*T. chui*)	9432.49	tonnes	-	From spray dryer	2
Inputs – Electricity/Heat					
Electricity, high voltage, Queensland/AU U	10375.74	GJ	-	Thermal decomposition energy input required @ 1.1 MJ/kg dry material'; ref Grierson et al 2009	1

B4.2 Scenarios 3 & 4:

Intermediary Processing (Direct oil extraction)

Name	Amount	Unit	Allocation (if any)	Comment	Data Quality*
Products & Co-products					
Algal oil extract (*T. chui*)	1377.14	tonnes	-	Solvent extracted, unrefined	2
Microalgae residue (*T. chui*)	8055.34	tonnes	-	Post-extraction residue	2
Inputs – Materials/Fuels					
Dry microalgae biomass (*T. chui*)	9432.49	tonnes	-	5% moisture	2
Organic solvent mix - MeOH:DCM (9:1)	70.74	tonnes	-	Closed system	2
Inputs – Electricity/Heat					
Electricity, high voltage, Queensland/AU U	5187.87	MWh	-	Solvent application and recovery system	3
Emissions to air					
Methane, dichloro-, HCC-30	10	kg	-	Based on 0.0015% loss; ref CSIRO 2007	3
Methanol	1.5	kg	-	Based on 0.0015% loss; ref CSIRO 2007	3

Production (Transesterification + slow pyrolysis)

Name	Amount	Unit	Allocation (if any)	Comment	Data Quality*
Products & Co-products					
Microalgae biodiesel	1543.26	tonnes	-	40 MJ/kg cf. rapeseed methyl ester	6 / 7
Microalgae residue – bio-oil	4543.21	tonnes	-	13.5 MJ/kg derived as per Fassinou 2012	3 / 7
Microalgae residue – biogas	394.71	tonnes	-	0.5 MJ/kg	1 / 7
Microalgae residue – biochar	1543.62	tonnes	-	14.5 MJ/kg	1 / 7
Inputs – Materials/Fuels					
Algal oil extract (*T. chui*)	1377.14	tonnes	-	Solvent extract @ 15%/wt of dry material	2
Microalgae residue (*T. chui*)	8055.34	tonnes	-	Post-extraction residue	2
Methanol/AU U	154.36	tonnes	-	Ref Batan et al 2010	3
Sodium methoxide, at plany/GLO U	19.3	tonnes	-	Ref Batan et al 2010	3
Sodium hydroxide, production mix, at plant/kg/RNA	7.72	tonnes	-	Ref Batan et al 2010	3
Hydrochloric acid from benzene chlorination, at plant/RER U	10.96	tonnes	-	Ref Batan et al 2010	3
Inputs – Electricity/Heat					
Electricity, high voltage, Queensland/AU U	8860.87	GJ	-	Thermal decomposition energy input required @ 1.1 MJ/kg dry material; ref Grierson et al 2009	1
Electricity, high voltage, Queensland/AU U	46.31	MWh	-	Ref Batan et al 2010	3
Energy, from natural gas/AU U	10	kg	-	Ref Batan et al 2010	3

B5. Use Phase

B5.1 Scenario 1: Electricity only

Name	Amount	Unit	Allocation (if any)	Comment	Data Quality*
Products & Co-products					
Electricity from pyrolysis of microalgae	35649	MWh	-	Consolidated electricity produced from pyrolysis co-products	1 / 7
Inputs – Materials/Fuels					
Electricity from bio-oil – sent out	30670	MWh	-	Based on 'RER Heavy Fuel Oil' (41.2 MJ/kg), assumes an energy value of 27.9 MJ/kg i.e. 1.48x impact/intensity of HFO	1 / 7
Electricity from biogas – sent out	211	MWh	-	Based on 'Electricity landfill gas, sent out/AU U' for the year 2001-02. The microalgal pyrolysis biogas energy content is taken as 2.5 MJ per kg or 10% of the landfill gas. Plant efficiency for power sent out is 30%. Based on power sent out therefore taking no account of transmission losses.	1 / 7
Electricity from biochar – sent out	4768	MWh	-	Based on 'Electricity brown coal SA (2001-02) sent out/AU U'; assumes an energy value of 14.5 MJ/kg biochar	1 / 7

B5.2 Scenario 2: Electricity and biochar (soil application)

Name	Amount	Unit	Allocation (if any)	Comment	Data Quality*
Products & Co-products					
Electricity from pyrolysis of microalgae	30881	MWh	83%	Consolidation of electricity produced from combustion of pyrolysis bio-oil and biogas.	1 / 7
Biochar applied to soil	3659.81	tonnes	17%	Bio-CCS & soil conditioning	1 / 7
Inputs – Materials/Fuels					
Electricity from bio-oil	30670	MWh	-	Based on 'RER Heavy Fuel Oil' (41.2 MJ/kg), assumes an energy	1 / 7

– sent out				value of 27.9 MJ/kg i.e. 1.48x impact/intensity of HFO	
Electricity from biogas – sent out	211	MWh	-	Based on 'Electrictiy landfill gas, sent out/AU U' for the year 2001-02. The microalgal pyrolysis biogas energy content is taken as 2.5 MJ per kg or 10% of the landfill gas. Plant efficiency for power sent out is 30%. Based on power sent out therefore taking no account of transmission losses.	1 / 7
Biochar production	3659.81	t	-		1 / 7
Biochar application to soil	3659.81	t	-	Based on 'solid manure loading and spreading, by hydraulic loader and spreader/kg/CH'	

B5.3 Scenario 3: Biodiesel and Electricity

Name	Amount	Unit	Allocation (if any)	Comment	Data Quality*
Products & Co-products					
Electricity from pyrolysis of microalgae residue	18014	MWh	16%		1 / 7
Biodiesel	1543.62	t	84%		3 / 7
Inputs – Materials/Fuels					
Electricity from residue bio-oil – sent out	13397	MWh	-	Based on 'RER Heavy Fuel Oil' (41.2 MJ/kg), assumes an energy value of 13.5 MJ/kg i.e. 3.05x impact/intensity of HFO	1 / 7
Electricity from residue biogas – sent out	16	MWh	-	Based on 'Electrictiy landfill gas, sent out/AU U' for the year 2001-02. The microalgal pyrolysis residue biogas energy content is taken as 0.5 MJ per kg or 2% of landfill gas. Plant efficiency for power sent out is 30%. Based on power sent out therefore taking no account of transmission losses.	1 / 7
Electricity from residue biochar – sent out	4061	MWh	-	Based on 'Electricity brown coal SA (2001-02) sent out/AU U'; assumes an energy value of 14.5 MJ/kg biochar	1 / 7
Articulated truck operation	66375.66	GJ		Based on CSIRO identifier 38818433900131	3 / 7

B5.4 Scenario 4: Biodiesel, electricity and biochar (soil application)

Name	Amount	Unit	Allocation (if any)	Comment	Data Quality*
Products & Co-products					
Electricity from pyrolysis of microalgae residue	13953	MWh	13%		1 / 7
Biochar applied to soil	3117.42	t	5%		1 / 7
Biodiesel from direct oil extraction	1543.62	t	83%		3 / 7
Inputs – Materials/Fuels					
Electricity from bio-oil – sent out	13937	MWh	-	Based on 'RER Heavy Fuel Oil' (41.2 MJ/kg), assumes an energy value of 13.5 MJ/kg i.e. 3.05x impact/intensity of HFO	1 / 7
Electricity from biogas – sent out	16	MWh	-	Based on 'Electrictiy landfill gas, sent out/AU U' for the year 2001-02. The microalgal pyrolysis residue biogas energy content is taken as 0.5 MJ per kg or 2% of landfill gas. Plant efficiency for power sent out is 30%. Based on power sent out therefore taking no account of transmission losses.	1 / 7
Articulated truck operation	66375.66	GJ		Based on CSIRO identifier 38818433900131	1 / 7
Biochar production	3117.42	t	-	From processing phase	1 / 7
Biochar application to soil	3117.42	t	-	Based on 'solid manure loading and spreading, by hydraulic loader and spreader/kg/CH'	

B6. Normalisation & Weighting Factors: Ecopoints + USEtox

Impact Category	Normalisation	Weighting*
Global Warming	0.000037	21
Eutrophication	0.053	3
Land use	0.034	17
Water use	0.0011	6
Human toxicity, cancer	2340	1.5
Human toxicity, non-cancer	326000	1.5
Ecotoxicity	0.00012	28
Acidification	0.009	4
Photochemical smog	0.013	3
Non-renewable fuel depl.	0.00006.36	3
Mineral depletion	0.000000033	4
Ozone depletion	548.3	4
Ionizing radiation	0.00076	2
Respiratory effects	0.02	3

* Weighting factors are rounded up to the nearest 0.5, hence adding up to a total of 101 points.

B7. Economic allocations

B7.1 Scenario 2: Electricity & biochar

Product	Production	Energy	Unit	Price	Value	Allocation
Bio-oil	4848.3	30670	MWh	$29.07		
Biogas	924.38	211	MWh	$29.07		
		30881	MWh	$29.07	$897,701	**83%**
Biochar	3659.81		tonnes	$50	$182,991	**17%**

B7.2 Scenario 3 Biodiesel & electricity

Product	Production	Energy	Unit	Price	Value	Allocation
Bio-oil	4534	13937	MWh	$29.07		
Biogas	350	16	MWh	$29.07		
Biochar	3117	4061	MWh			
		17474	MWh	$29.07	$897,701	**83%**
Biodiesel	1544		tonnes	$1,727	$2,666,488	**17%**

B7.3 Scenario 4 Biodiesel, electricity & biochar

Product	Production	Energy	Unit	Price	Value	Allocation
Bio-oil	4534	13937	MWh	$29.07		
Biogas	350	16	MWh	$29.07		
		13953	MWh	$29.07	$405,614	**13%**
Biochar	3117		tonnes	$50	$155,850	**5%**
Biodiesel	1544		tonnes	$1,727	$2,666,488	**83%**

B8. Infrastructure Calculations

The following provides a breakdown of infrastructure items considered analogous to the microalgae and pyrolysis value chain, taken from the Ecoinvent database. This is to demonstrate that over an assumed design life of 30 years, capital infrastructure items can be reasonably excluded from the study, having 3% or less contribution to make to overall impact.

Infrastructure Item	#	Unit	Ecopoints (Life)	Comments
Vegetable oil esterification plant	1	plant	5,787	Included processes: This process includes land use and occupation, buildings and facilities of a typical industrial vegetable oil esterification plant in the Swiss context. Energy use for construction and related emissions and/or waste effluents are not included. Remark: Esterification plant with a daily production of 63 t methyl ester. Life time of plant taken as 50 years. Technology: Typical vegetable oil esterification plant designed for methyl ester production (for use in the vehicle fuels market) adapted to Swiss conditions and context, CH, vegetable oil base-catalyzed transesterification facility.
Wastewater treatment plant, class 5	1	plant	1,442	Included processes: Infrastructure materials for municipal wastewater treatment plant, transports, dismantling. Land use burdens. Remark: For municipal wastewater treatment plant capacity class 5 with an average per-captia equivalent PCE (Einwohnergleichwert) of 806 and an average annual sewage volume of 163'000 m3/a. A lifetime of 30 years is assumed.; Geography: Specific to the technology mix encountered in Switzerland in 2000. Well applicable to modern treatment practices in Europe, North America or Japan. Technology: Three stage wastewater treatment (mechanical, biological, chemical) including sludge digestion (fermentation).
Pipe, DN250 PE PN8, installed underground	100	km	14,365	

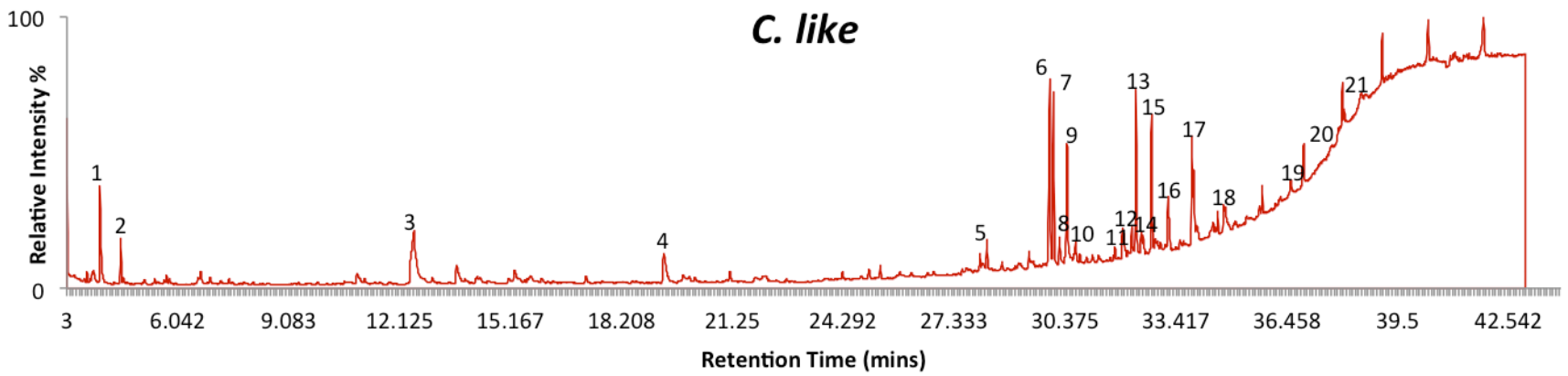
Sugar Refinery	1	plant	25,930	Included processes: This process includes land use and occupation, buildings and facilities of a typical sugar refinery in the global context. Energy use for construction and related emissions and/or waste effluents are not included.Remark: Sugar refinery with a production capacity of 200 kt sugar per year (production period of 100-180 days/year, depending on the feedstock). Life time is taken as 50 years. Equivalent feed capacities vary from 1'300 kt/yr for sugar beets to 1'650 kt/yr for sugarcane.; Geography: Global context. Applicable to any sugar refinery in the world. Technology: Technology is of a standard sugar refinery, including washing of the feedstock, juice extraction, purification and crystallisation. Juice extraction is performed by diffusion.
Pipe, PVC 50mm drainage pipe, at regional store	100	km	1,077	
Water pump 5.5kW- 60kg	1000	pump	237	
Small pump for water tank	1000	pump	79	
Total over 30 years (Ecopoints)			49,918	

B8.1 Results Summary

Product	Time	Unit	Ecopoints (Life)	Relative Impact of infrastructure
Dry algae biomass	30	yr	1,394,250	3.0%
SC1: Electricity	30	yr	1,948,440	2.6%
SC2: Electricity & Biochar	30	yr	1,888,620	2.6%
SC3: Biodiesel & Electricity	30	yr	2,520,930	2.0%
SC4: Biodiesel, Electricity & Biochar	30	yr	2,724,480	1.8%

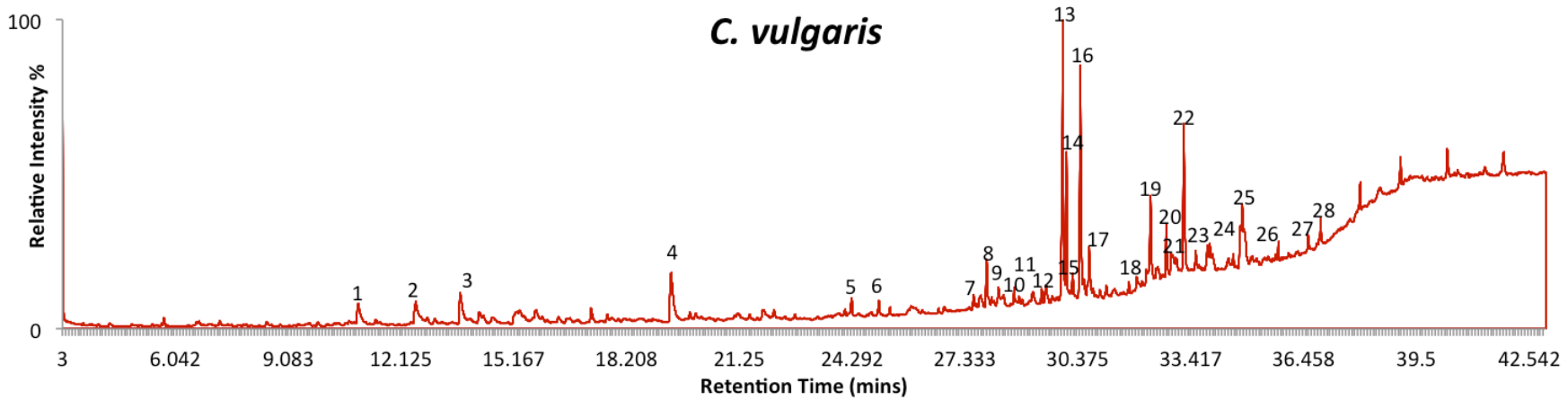
Appendix C: Additional GC-MS data relating to pyrolysis liquids

The following presents the biochemical composition of bio-oils produced by GC-MS for the additional microalgae species examined in Chapter 3. The decision not to publish this additional information previously was based solely on the limitation and availability of sufficient dry biomass samples from which a comprehensive set of complimentary analytical data could be gathered. Since GC-MS analysis only requires a small amount of liquid to be analysed, this was the only reliable test that could be carried out with sufficient scope for replicates across all species.



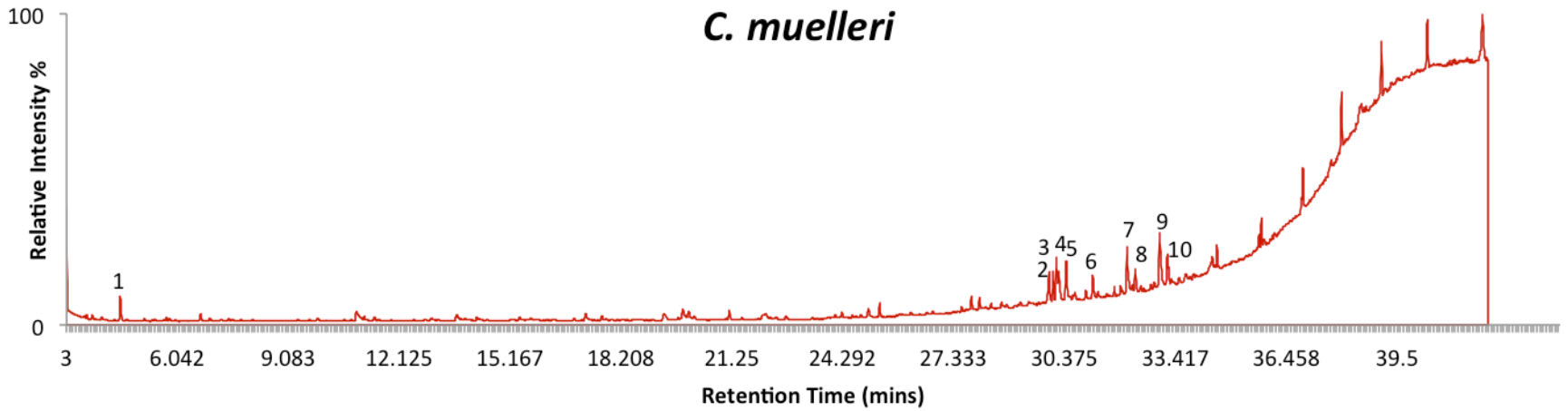
Key	Ret. Time	Name	Formula	Area %
1	3.906	Pyridine	C_5H_5N	3.89
2	4.475	Toluene	C_7H_8	1.55
3	12.518	2-Pyrrolidinone	C_4H_7NO	7.1
4	19.37	5H-1-Pyridine	C_8H_7N	3.12
5	28.227	Pentadecane	$C_{15}H_{32}$	1.72
6	29.95	3,7,11,15-Tetramethyl-2-hexadecen-1-ol	$C_{20}H_{40}O$	8.86
7	30.051	2-Hexadecene, 3,7,11,15-tetramethyl-, [R-[R@,R@-(E)]]-	$C_{20}H_{40}$	5.88
8	30.219	3,7,11,15-Tetramethyl-2-hexadecen-1-ol	$C_{20}H_{40}O$	1.46
9	30.428	Pentadecanal-	$C_{15}H_{30}O$	6.67
10	30.664	Tridecanal	$C_{13}H_{26}O$	1.21
11	31.943	5-Dodecyne	$C_{12}H_{22}$	1.14
12	32.202	Pentanoic acid, 10-undecenyl ester	$C_{16}H_{30}O_2$	0.78
13	32.313	Octadecanoic acid, 2-propenyl ester	$C_{21}H_{40}O_2$	6.45
14	32.464	Z-15-Octadecen-1-ol acetate	$C_{20}H_{38}O_2$	0.99
15	32.74	Phytol	$C_{20}H_{40}O$	5.52
16	33.196	Hexadecanamide	$C_{16}H_{33}NO$	3.58
17	33.85	9,17-Octadecadienal, (Z)-	$C_{18}H_{32}O$	9.15

18	34.721	7,10-Hexadecadienoic acid, methyl ester	$C_{17}H_{30}O_2$	2.64
19	36.564	Pyrrolidine, 1-(1-oxooctadecyl)-	$C_{22}H_{43}NO$	0.61
20	37.858	Pyrrolidine, 1-(1-oxo-9,11-octadecadienyl)-, (Z,Z)-	$C_{22}H_{39}NO$	0.48
21	38.026	9-Octadecenamide, (Z)-	$C_{18}H_{35}NO$	0.6

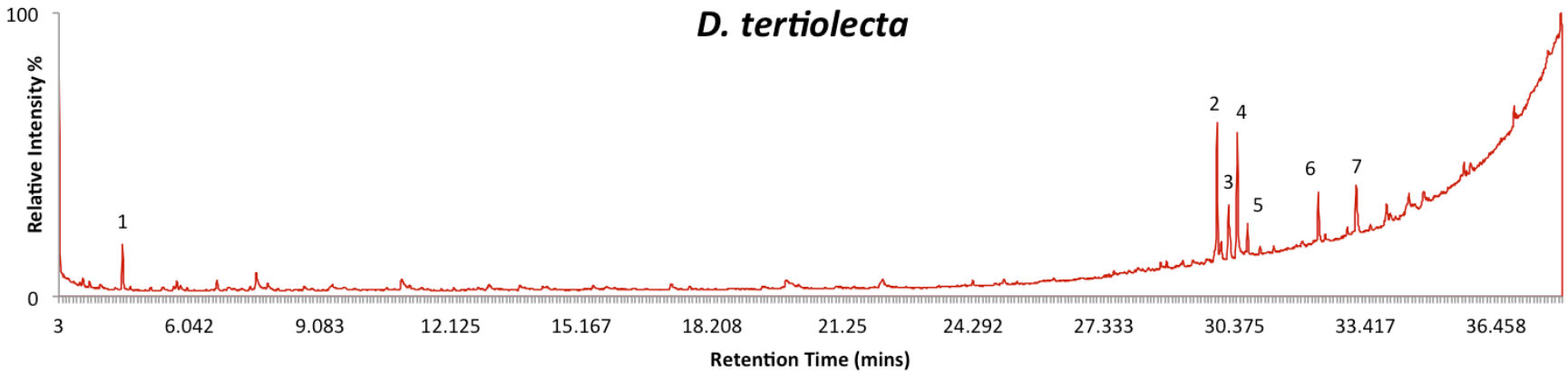


Key	Ret. Time	Name	Formula	Area %
1	10.966	Phenol	C_6H_6O	3.76
2	12.527	2-Pyrrolidinone	C_4H_7NO	3.49
3	13.724	Phenol, 4-methyl-	C_7H_8O	3.3
4	19.41	5H-1-Pyrindine	C_8H_7N	4.5
5	24.276	Hexadecane	$C_{16}H_{34}$	0.53
6	25.009	Tetradecane	$C_{14}H_{30}$	0.5
7	27.561	Pentadecane, 2,6,10-trimethyl-	$C_{18}H_{38}$	0.48
8	27.755	3-Pyrrolidin-2-yl-propionic acid	$C_7H_{13}NO_2$	1.11
9	28.237	Hexadecane	$C_{16}H_{34}$	0.96
10	28.372	10-Methyl-octadec-1-ene	$C_{19}H_{38}O$	0.89
11	28.656	1-Dodecanol, 3,7,11-trimethyl-	$C_{15}H_{32}O$	0.62
12	29.397	1-Decanol, 2-hexyl-	$C_{16}H_{34}O$	0.37
13	29.965	3,7,11,15-Tetramethyl-2-hexadecen-1-ol	$C_{20}H_{40}O$	10.01
14	30.064	2-Hexadecene, 3,7,11,15-tetramethyl-, [R-[R@,R@-(E)]]-	$C_{20}H_{40}O$	4.55
15	30.232	3,7,11,15-Tetramethyl-2-hexadecen-1-ol	$C_{20}H_{40}O$	1.06
16	30.441	Pentadecanal-	$C_{15}H_{30}O$	9.13
17	30.68	Undecane, 2-cyclohexyl-	$C_{17}H_{34}$	2.4
18	32.22	Cyclodecene	$C_{10}H_{18}$	0.67

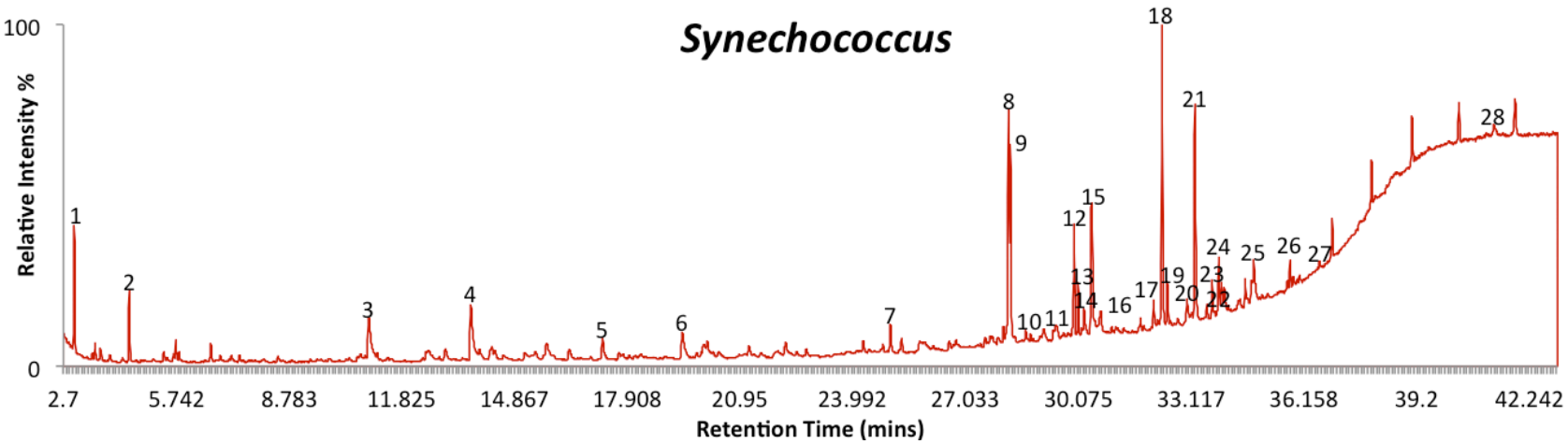
19	32.328	Octadecanoic acid, 2-propenyl ester	$C_{21}H_{40}O_2$	4.07
20	32.756	Phytol	$C_{20}H_{40}O$	1.97
21	32.886	9-Octadecenamide, (Z)-	$C_{18}H_{35}NO$	0.79
22	33.23	Hexadecanamide	$C_{16}H_{33}NO$	5.81
23	33.548	Dodecanal, o-methyloxime	$C_{13}H_{27}NO$	0.78
24	33.866	Isopropyl linoleate	$C_{12}H_{32}O_2$	0.95
25	34.805	8,11,14-Eicosatrienoic acid, (Z,Z,Z)-	$C_{20}H_{34}O_2$	2.45
26	34.858	9-Octadecenamide, (Z)-	$C_{18}H_{35}NO$	2.42
27	36.583	Pyrrolidine, 1-(1-oxooctadecyl)-	$C_{22}H_{43}NO$	0.5
28	37.883	Pyrrolidine, 1-(1-oxo-11, 14-eicosadienyl)-	$C_{24}H_{43}NO$	0.33



Key	Ret. Time	Name	Formula	Area %
1	4.476	Toluene	C_7H_8	1.89
2	29.951	3,7,11,15-Tetramethyl-2-hexadecen-1-ol	$C_{20}H_{40}$	3.44
3	30.057	2-Hexadecene, 3,7,11,15-tetramethyl-, [R-[R@,R@-(E)]]-	$C_{20}H_{40}$	2.35
4	30.151	E-9-Tetradecanal	$C_{14}H_{26}O$	7.71
5	30.417	Hexadecanenitrile	$C_{16}H_{31}N$	5.56
6	31.15	Hexadecanamide	$C_{16}H_{33}NO$	2.51
7	32.092	13-Octadecenal, (Z)-	$C_{18}H_{34}O$	5.56
8	32.316	Octadecanoic acid, 2-propenyl ester	$C_{21}H_{40}O_2$	3.19
9	32.986	9-Octadecenamide, (Z)-	$C_{18}H_{35}NO$	7.66
10	33.191	Hexadecanamide	$C_{16}H_{33}NO$	3.8



Key	Ret. Time	Name	Formula	Area %
1	4.479	Toluene	C_7H_8	3.3
2	29.958	3,7,11,15-Tetramethyl-2-hexadecen-1-ol	$C_{20}H_{40}O$	10.47
3	30.228	3,7,11,15-Tetramethyl-2-hexadecen-1-ol	$C_{20}H_{40}O$	5.23
4	30.436	Pentadecanal-	$C_{15}H_{30}0$	10.72
5	30.674	m-Menth-1(7)-ene, (R)-(-)-	$C_{10}H_{18}$	1.91
6	32.321	Octadecanoic acid, 2-propenyl ester	$C_{21}H_{40}O_2$	3.64
7	33.201	Hexadecanamide	$C_{16}H_{33}NO$	4.16



Key	Ret. Time	Name	Formula	Area %
1	2.925	Benzene	C_6H_6	0.3
2	4.476	Toluene	C_7H_8	2.06
3	10.932	Phenol	C_6H_6O	3.2
4	13.683	Phenol, 4-methyl-	C_7H_8O	4.21
5	17.241	Hydrazinecarboxylic acid, phenylmethyl ester	$C_8H_{12}N_2O_2$	1.11
6	19.386	Indolizine	C_8H_7N	1.9
7	25.002	Pentadecane	$C_{15}H_{32}$	0.99
8	28.188	Cyclopentane, 1,1'-[4-(3-cyclopentylpropyl)-1,7-heptanediyl]bis-	$C_{25}H_{46}$	8.07
9	28.235	Hexadecane, 2-methyl	$C_{17}H_{36}$	5.63
10	28.649	1-Nonanol, 4,8-dimethyl-	$C_{11}H_{24}O$	0.3
11	29.13	6-Oxabicyclo[3.1.0]hexan-3-one, 2,2,4,4,-tetram	$C_9H_{14}O_2$	1.11
12	29.957	3,7,11,15-Tetramethyl-2-hexadecen-1-ol	$C_20H_{40}O$	3.64
13	30.058	2-Hexadecene, 3,7,11,15-tetramethyl-, [R-[R@,R@-(E)]]-	$C_{20}H_{40}$	1.36
14	30.227	3,7,11,15-Tetramethyl-2-hexadecen-1-ol	$C_{20}H_{40}O$	1.23
15	30.426	Octadecanal	$C_{18}H_{36}O$	6.19
16	30.67	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)-	$C_{11}H_{18}N_2O_2$	1.46
17	32.094	Dodecane, 1-cyclopentyl-4-(3-cyclopentylpropyl)-	$C_{25}H_{48}$	1.05

18	32.322	Octadecanoic acid, 2-propenyl ester	$C_{21}H_{40}O_2$	9.06
19	32.469	Hexadecanoic acid, propyl ester	$C_{19}H_{38}O_2$	1.34
20	32.995	9-Octadecenamide, (Z)-	$C_{18}H_{35}NO$	1.04
21	33.209	Hexadecanamide	$C_{16}H_{33}NO$	8.33
22	33.531	Decanal, O-methyloxime	$C_{11}H_{23}NO$	0.41
23	33.677	Methyl (Z)-5,11,14,17-eicosatetraenoate	$C_{21}H_{34}O_2$	1.23
24	33.856	1,E-11,Z-13-Octadecatriene	$C_{18}H_{32}$	1.9
25	34.794	Octadecanoic acid, 3-hydroxypropyl ester	$C_{21}H_{42}O_3$	3.16
26	35.862	Hexadecanoic acid, 1-[[[(2-aminoethoxy)hydroxyphosphinyl]oxy]methyl]-1,2-ethanediyl ester	$C_{37}H_{74}NO_8P$	0.37
27	36.57	Pyrrolidine, 1-(1-oxooctadecyl)-	$C_{22}H_{43}NO$	0.23
28	41.277	Lupan-3-ol, acetate	$C_{32}H_{54}O_2$	0.57