
THE UNIVERSITY of ADELAIDE

# DIRECT CONVERSION OF MICROALGAE BIOMASS TO BIOCRUDE WITH HYDROTHERMAL LIQUEFACTION

BLESSING ELO-OGHENE EBOIBI

THESIS SUBMITTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

SCHOOL OF CHEMICAL ENGINEERING

FACULTY OF ENGINEERING, COMPUTER & MATHEMATICAL SCIENCES

THE UNIVERSITY OF ADELAIDE, AUSTRALIA

MAY, 2015

# Table of contents

# Executive Summary

Microalgae are generally considered as a promising biomass source for applications including production of advanced biofuels, chemicals, wastewater treatments, various organic substances or a combination of any of the above. The advantages of microalgae includes faster growth rates than terrestrial plants, ability to use non-arable land for mass production, and their ability to grow in poor quality water, as well as their ability to remove pollutants from wastewater streams. However, one of the major challenges of microalgae for commercialisation to is its economic downstream production and conversion to biofuels and chemicals. When harvested, microalgae contains up to ~90% water content, thus economic conversion of high moisture content biomass to valuable products such as biofuels remains a challenge. Hydrothermal liquefaction (HTL) involves processing of high moisture content biomass in hot compressed water, avoiding the drying step for biomass feedstocks. Therefore HTL is advantageous as it avoids the energy intensive drying process in contrast to processes that involve drying of biomass prior to processing into biofuels.

HTL products comprise biocrude, solid residues, aqueous and gas phases. The primary product biocrude is upgradable to liquid transportation fuels. The aqueous phase contains essential nutrients that could be recycled to microalgae cultivation ponds. The gas phase contains about 98mol% carbon dioxide ($CO_2$) and 2mol% hydrocarbon gases. The gas phase can also be directly recycled to the microalgae cultivation ponds for pH control and supply of $CO_2$, thus, reducing production costs. Aside from the feedstock selection, maximising yield and improving the quality of biocrude, achieving an energy positive, low carbon footprint and economic viability are important challenges facing a HTL-microalgae-biofuels system. In addition, the biocrude must meet refining specifications, for example, it needs to be high in carbon and hydrogen, low nitrogen, oxygen, sulphur, and have a high energy density similar to conventional crude oils.

This thesis was on optimisation studies to quantify process parameters. Process parameters such as reaction temperature, reaction time, feedstock, catalyst selection, solvent type for maximum yield and improved quality biocrude have been investigated. A halophytic microalga *Tetraselmis* sp. was investigated in this study. The investigation was performed at different reaction temperatures 310$^{o}$C, 330$^{o}$C, 350$^{o}$C, and 370$^{o}$C at reaction times of 5min, 15min, 30min, 45min, and 60min with a fixed 16%w/w microalgae biomass solid content

feedstock. This investigation showed that the operating conditions to achieve maximum biocrude yield and ideal quality biocrude for refining were different. The obtained biocrude yields were in the range 35wt% to 68wt% (ash free dry weight), the maximum achieved at a reaction temperature of 350$^{o}$C and a 5min reaction time. High yields of biocrude were achieved by short reaction times, whilst better quality biocrude were achieved at long reaction times. The biocrude was found to contain undesired high amounts of heteroatoms, particularly nitrogen and oxygen and metallic impurities. Thus the resultant biocrude cannot be directly applied as transportation fuels. For transportation purposes, the biocrude will need to be upgraded to remove the heteroatoms or used for boiler firing or blended with fossil crude. The biocrude exhibited higher heating value (HHV) of 28MJ/kg to 39MJ/kg similar in nature to petroleum crude. The C, H, N, S, and O content were in the range 67%w/w to 79%w/w (carbon), 6%w/w to 9.5%w/w (hydrogen), ~4%w/w to 6.5%ww/w (nitrogen), 0.5%w/w to 0.9%w/w (sulphur) and 6%w/w to 21.6%w/w for oxygen.

Due to the high concentration of nitrogen in the resultant biocrude, an alternative to direct HTL involving pretreatment of biomass with the extraction of protein prior to further processing of the resultant residue to biocrude was performed. The influence of process conditions during both pre-treatment for protein extraction and HTL of the pre-treated *Tetraselmis* sp. for biocrude production was investigated. The pretreatment step was shown to extract protein which could be used as valuable by-products. The extraction was shown to improve the quality of the resultant treated microalgae biomass, as the amounts of nitrogen content were reduced. HTL of the pretreated microalgae led to a maximum biocrude yield of 65wt% at 310$^{o}$C, 30min which was more than a 50% improvement in yield as compared to HTL of untreated microalgae at the same reaction conditions. To achieve a similar biocrude yield using the untreated biomass required a much higher reaction temperature of 350$^{o}$C. Using recycled HTL aqueous phase as reaction media led to a 25wt% higher biocrude yield. HTL of pre-treated microalgae biomass led to 32% to 46% nitrogen reduction in the resultant biocrude. A maximum of 15wt% protein extract was obtained during microalgae pre-treatment at 150$^{o}$C, 20min. A similar energy input was required in biocrude production from untreated route and the combined pre-treatment and HTL.

The effect of seawater as reaction media during hydrothermal liquefaction of microalgae was investigated. Different seawater concentrations containing varying amounts of dissolved salt

were employed and the results compared to deionised water. It was found that seawater could improve the biocrude yield, however, with no substantial enhancement in properties.

Products yields and properties from the HTL of freshly harvested microalgae biomass slurry and diluted pulverised microalgae biomass were compared. The results show higher biocrude yields could be obtained from fresh biomass slurry than diluted pulverised biomass. In addition, lower yields in solid residue and aqueous phase were obtained from fresh biomass slurry compared to diluted pulverised biomass. However, there was no substantial difference in the properties of biocrude from the different feedstocks.

Improving the quality of HTL biocrude without the application of a catalyst or hydrogen was performed with vacuum distillation. In addition to the primary product (distilled biocrude), the distillate contained a substantial amount of solid residue and water. Vacuum distillation of HTL biocrude led to 62wt% to 67wt% and 70wt% to73wt% of distilled-biocrude from *Spirulina* sp. and *Tetraselmis* sp. biocrudes, respectively. It was shown that the higher heating value (HHV) increased from 32MJ/kg to ~40MJ/kg following distillation. About 83% carbon and 78% energy was recovered in the distilled biocrudes from HTL biocrudes feed. The results show improved quality biocrude as there were significant reductions in oxygen and metallic contents, and boiling point range in the distilled biocrudes.

A concept for integrating anaerobic digestion (AD) and hydrothermal liquefaction for waste management to recover residual carbon was investigated by processing the AD digestate via HTL. The results show the feasibility to recover residual carbon from organic waste producing valuable product biocrude. An average biogas yield of $0.5 m^3/kgVS_{added}$ was obtained following anaerobic digestion at different hydraulic retention times (HRTs). The HTL of the resultant effluents seem to vary with HRTs, and a maximum biocrude yield of 42wt% was achieved. It was found that up to 76% and ~ 70% carbon and energy can be recovered in the biocrude. Importantly, the resultant biocrude was found to have very low nitrogen content similar to that of petroleum crude.

The outcome of this study will provide fundamental data for a commercial development of HTL microalgae biofuels. One of the major outcomes of this work is the feasibility to produce high yields in biocrude at a very short reaction time (5min) and importantly under subcritical condition. The high yields obtained from *Tetraselmis* sp. will significantly

improve the life-cycle analysis and the viability of HTL microalgae biofuels. The demonstrated ability of microalgae pretreatment prior to HTL is a potential means to simultaneously to obtain a co-product alongside the primary product biocrude. The revenue derived from the co-products will also improve the economics of HTL. Moreover, the idea of using recycled pretreatment process water as HTL reaction media is a significant contribution as it leads to a higher biocrude yield. The use of natural seawater as a reaction media is novel as it avoids employing organic solvents, saving associated cost and freshwater. It was found that the use of catalyst for upgrading of biocrude, improving its HHVs and molecular weight is not necessarily required, since similar upgraded biocrude yields and fuel properties were achieved following vacuum distillation of biocrude.

# Declaration

I certify that this work contains no material which has been accepted for the award of any other degree or diploma in my name in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in text. In addition, I certify that no part of this work will, in the future, be used in a submission in my name for any other degree or diploma in any university or other tertiary institution without the prior approval of the University of Adelaide and where applicable, any partner institution responsible for the joint award of this degree.

I give consent to this copy of my thesis when deposited in the University Library, being made available for loan and photocopying, subject to the provisions of the Copyright Act 1968.

The author acknowledges that copyright of published works contained within this thesis resides with the copyright holder(s) of those works.

I also give permission for the digital version of my thesis to be made available on the web, via the University's digital research repository, the Library Search and also through web search engines, unless permission has been granted by the University to restrict access for a period of time.

_____ _____

Blessing Eboibi Date

# Acknowledgements

I would like to acknowledge my supervisors Associate Prof David Lewis, Prof Peter Ashman and Dr Senthil Chinnasamy. I am especially grateful for all their understanding, patience, constant guidance, valuable and constructive criticism and assistance throughout my PhD.

I highly appreciate the financial support received from the Australian Research Council's Linkage Projects funding scheme (LP100200616) with industry partner SQC Pty Ltd and the Australian Renewable Energy Agency (ARENA) advanced biofuels readiness program. I would like to acknowledge the financial support I have received in the form of a Postgraduate Scholarship from the Education Trust Fund of the Federal Republic of Nigeria.

I wish to thank past and current members and PhD colleagues of the Microalgal Engineering Research Group: Kwong Shui Andrew Lee, Sanaz Orandi, Sophie Fan Sing, Stephen Pahl, Amir Foghani, Andrew Ward, Mason Erkelens, Steven Amos, Theo Kalaitzadis, Wynand Van den Berg, Quang Doan. I would like to thank past and present School of Chemical Engineering Office members of staff: Elaine Minerd, Mary Barrow, Gemma Higgs, Monica Dinan and Sue Earle for all their administrative assistance during my PhD Programme. I am grateful to Dr Michelle Picard for the editorial assistance.

The laboratory and technical assistance provided by members of staff, Aban Infrastructure Pvt. Ltd, Biotechnology Division India was greatly appreciated. I would especially thank Prof S Sivasenka and his team at the National Centre for Catalysis Research, India Institute of Technology, Chennai, India. Special thanks to members of staff of the Research and Development, Chennai Petroleum Cooperation Ltd, India. I am also grateful to members of staff at the Central Leather Research Institute, Pilot Plant, Chennai, for the technical and laboratory assistance.

Finally, my heart goes to my wife, and beautiful daughter Cherish Eboibi for their love, emotional support and encouragement throughout my PhD period. I thank Cherish for her patience and understanding of me not being fully with her during this gruelling process. I would like to thank my parents Mr and Mrs Lucky Eboibi (JP), grandmother, brothers and sisters. I am grateful for all your immeasurable love and support. I am also grateful to all friends and well-wishers for their care and support, thank you.

# Preface

This thesis is submitted as a portfolio of publications according to the "Specifications for Thesis 2014" of the University of Adelaide. The journals in which the papers were published or submitted have high impact factors in the field of Chemical Engineering. Data on the impact factors of the journals are listed below:

| Journal Title | Impact Factors | |
|---|---|---|
| | 2015 | 5 year |
| Bioresource Technology | 5.03 | 5.60 |
| RSC Advances | 3.70 | 3.70 |
| Fuel Processing Technology | 3.02 | 3.70 |
| Environmental Progress & Sustainable Energy | 1.27 | 1.55 |

The main intellectual contribution of this thesis has been published in the following five journal papers:

1. Eboibi, BE, Lewis, DM, Ashman, PJ & Chinnasamy, S 2014, 'Effect of operating conditions on yield and quality of biocrude during hydrothermal liquefaction of halophytic microalga *Tetraselmis* sp', *Bioresource Technology*, 170, 20-29.

2. Eboibi, BE, Lewis, DM, Ashman, PJ & Chinnasamy, S 2014, 'Hydrothermal liquefaction of microalgae for biocrude production: Improving the biocrude properties with vacuum distillation', *Bioresource Technology*, 174, 212-221.

3. Eboibi, BE, Lewis, DM, Ashman, PJ & Chinnasamy, S 2015, 'Influence of process conditions on pre-treatment of microalgae for protein extraction and the production of biocrude during hydrothermal liquefaction of pre-treated *Tetraselmis* sp.', *RSC Advances*, 5, 20193-20207.

4. Eboibi, BE, Lewis, DM, Ashman, PJ & Chinnasamy, S 'Effect of seawater and wet feedstock on product distribution and properties during hydrothermal liquefaction of microalgae', *Fuel Processing Technology*, Under review.

5. Eboibi, BE, Lewis, DM, Ashman, PJ & Chinnasamy, S 'Integrating anaerobic digestion and hydrothermal liquefaction for renewable energy production: An experimental investigation', *Environmental Progress & Sustainable Energy*, Under review.