



Technical issues in the large-scale hydrothermal liquefaction of microalgal biomass to biocrude

Andrew Lee^{1,3}, David Lewis^{1,2,3}, Theo Kalaitzidis¹ and Peter Ashman^{1,3}

Much of the current knowledge on the hydrothermic liquefaction of biomass to biocrude is on the basis of laboratory benchtop findings, and the step up to industrial scale reactors will require a range of information that is currently either unavailable or insufficient. This work highlights a number of these issues such as the heat of reaction, process heat recovery, optimal reaction time and waste product treatment. Effects of these knowledge gaps on the reactor design, process economics, and impacts on the environment are discussed. Although technologies do exist to deal with some of these issues, their applications are often limited by economic considerations and further studies are required.

Addresses

¹ Microalgal Engineering and Research Group, School of Chemical Engineering, University of Adelaide, SA, Australia

² Muradel Pty Ltd, Suite 1, 1401 Burke Road, Kew East, Vic 3102 Australia

³ Centre for Energy Technology, University of Adelaide, SA, Australia

Corresponding author: Lee, Andrew (alee@chemeng.adelaide.edu.au)

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Introduction

Microalgae has been investigated as a potential feedstock for the production of biofuels [1] and hydrothermal liquefaction, HTL, is able to convert wet biomass, such as freshly harvested microalgae, directly to biocrude [2]. The conversion is carried out under subcritical water range of temperature, °C, of 300–370 and pressure, MPa, of 20–23 and the process has a lower energy requirement than the extraction and transesterification of lipids [3]. Currently, the vast majority of studies on microalgal HTL were on the basis of small laboratory batch reactors, and the reports on continuous reactors were limited to a few researchers [4,5]. In addition, large-scale production issues such as the process energy consumption, reactor design and waste product treatment

are often overlooked. This study identifies and discusses some of the issues specifically associated with the large scale microalgal HTL.

Technical issues in a large-scale microalgal HTL

The enthalpy change of HTL reaction, ΔH

Reactors for either endothermic or exothermic reactions require different heat transfer systems for the supply or removal of heat, and reactors are designed accordingly; however, the enthalpy change of HTL reactions, ΔH , has not yet been determined experimentally. Values of ΔH , which are expected to vary according to feedstock characteristics and reaction conditions, are particularly important in designing large-scale continuous reactors where:

- i. Low economic values of biocrude require all resources, including the processing energy requirement, to be optimised,
- ii. Reactor temperatures need to be controlled within a range of few °C under the critical water temperature of approximately 370 °C to achieve the maximum reaction rate and biocrude yield.

The data available from literature appears to be rather limited and inconsistent; the overall reaction has been reported to be either endothermic with a ΔH value of +84 kJ kg⁻¹ [6], or mildly exothermic without quoting any value [7,8]. The unknown value of ΔH makes it difficult to design a commercial scale reactor with a proper heat transfer system.

Process heat recovery

The high critical water temperature of 375 °C and operating pressure of over 22 MPa require a substantial input of processing heat that need to be recovered downstream by heat exchangers; however, unprocessed microalgal biomass with a dry mass content of 15–20% has a paste-like consistency and behaves as a non-Newtonian fluid [9]. The high viscosity results in poor heat transfer characteristics and a relatively large heat exchange area will be required to maximise the heat recovery. In addition, the reactor and heat exchanger require walls of sufficient thickness to withstand the high temperature and pressure during HTL, for example, the standard 3 inch stainless steel SS316 pipe rated at 20 MPa at 325 °C has a wall thickness of 15.2 mm. This wall thickness will further reduce the heat recovery efficiency. For

laboratory HTL, the reaction temperatures and duration can easily be controlled by excessive heat supply and quenching the sealed reactors, but the heat consumed is not recoverable.

The large surface area requirement, high operation temperature and pressure, together with the low energy recovery, will increase the cost of construction and maintenance of the HTL reactor.

Reaction time for the optimal yield and quality

In large-scale HTL reactors, due to the limitations in heat transfer (See section 'Process heat recovery'), the bulk temperature of reactants require a period of time to be raised from ambient to that of the HTL. During such time period, carbonisation, which occurs at the temperature range of 250–300 °C, converts the biomass to char and tar like particles and reduces the biocrude yield [10,11]. In industrial processing, where thermal energies are usually recovered by heat exchangers, the rise in reactant temperature will be much slower than that can be achieved in the laboratory (See section 'Process heat recovery') and carbonisation will reduce the yield.

In addition to problems associated with carbonisation, longer reaction times would require larger reactors which suffer from higher construction cost, require more mixing energy and higher heat transfer capacities. A larger HTL reactor that operates at a relatively high temperature range of (300–350) °C also suffers from higher thermal energy loss via convection and radiation. Again, a range of reaction times have been reported by different authors: the reported reaction times with respect to the optimal yield, using continuous HTL reactors, ranged from a low of 0.5 min to a high of 40 min [4^{**},5^{**},12,13]; in addition, the time to achieve both the optimal yield and quality remains to be optimised. The uncertainty in reaction times makes it difficult to determine a reactor size suitable for large-scale HTL.

Pickering emulsion

A Pickering emulsion is one that is stabilised by fine solid particles. During HTL, particles of clay, aluminosilicate and bio-char are present, these particles stabilise the oily crude between the solid/aqueous interphase and is difficult to separate. When microalgal feedstock is used, the high level of nitrogenous compounds formed further stabilises the emulsion in a manner similar to that occurs in tar sands. Currently, the oily phase of the emulsion can be separated from the solid by solvent extraction [5^{**},14], but the amount of solvents and energy consumed during the extraction makes this process impractical.

In a continuous HTL reactor, emulsification appears to occur upon product depressurisation at a lower temperature region located towards the end of the reactor; hence, the separation (such as settling) of solids upstream in the

region of high temperature and high pressure will be able to mediate the emulsion formation at a later stage [6^{*},15]. Further studies are required for a more efficient biocrude/solid separation.

Corrosion

HTL produces a range of oxygenated and/or chlorinated compounds including organic acids and aldehydes. These chemicals, in the presence of dissolved mineral ions and high temperature, create a corrosive environment. Major types of corrosion include hydrogen embrittlement, pitting, inter-crystalline and metal stress fatigue. Commonly used reactor construction materials for subcritical applications are usually Ni alloys such as SS304. Corrosion weakens the metal grain structure [16] and cause the leaching of reactor metals, creating water recycling and waste disposal issues (See section 'Minor issues'). Technically, corrosion is not an unsurmountable obstacle but it adds to the construction cost [17,18].

Nitrogen reduction

The high protein content of microalgae gives rise to high N levels of (3–8) wt.% in the biocrude, causing a range of problems such as high viscosity, catalyst deactivation and NO_x emission [19^{**}]. These N-complexes can be reduced by the removal of protein before HTL processing:

- A two-stage HTL with the first stage operating at a lower temperature of 200 °C to remove the protein, followed by a higher temperature second stage of up to 350 °C to complete the HTL [20]; however, the removal of N-complexes results in a lower crude yield.
- The use of N-adsorbent such as Al₂(SO₄)₃ with the N being recovered by extraction with benzene [21]; however, the problem still exists with the amount of N remaining in the benzene.
- The fractionation of the algal biomass by step-wised acid and base hydrolysis, followed by solvent extraction and centrifugation. This process has the advantage of utilising more of the biomass but the complexity of the process may not be commercially viable [22].

Currently there is no economical and efficient N removal method.

Biocrude upgrading

Biocrude is a dark brown oily liquid and requires upgrading to be suitable as transport fuels [23,24]. The upgrading includes [25–27]:

- Filtration or settling to remove solid particles.
- Catalytic hydro-treating such as NiMo to reduce the presence of O, N and S.
- Cracking, decarboxylation or aromatisation by molecular sieves such as ZSM-5 at (300–500) °C.
- Blending with diesel and surfactant (e.g. Hypermer) to reduce viscosity.

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