



Hydrothermal upgrading of algae paste: Inorganics and recycling potential in the aqueous phase



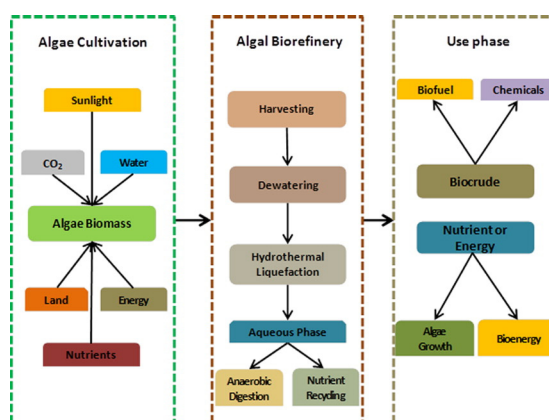
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HIGHLIGHTS

- HTL of algal biomass and nutrient reclamation
- Microalgae HTL aqueous phase inorganics analysis
- Recycle/re-use of aqueous phase for energy or cultivation
- Substantial environmental benefit from HTL of aqueous phase
- Reuse for cultivation more beneficial than Anaerobic Digestion

GRAPHICAL ABSTRACT



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ABSTRACT

Hydrothermal Liquefaction (HTL) for algal biomass conversion is a promising technology capable of producing high yields of biocrude as well as partitioning even higher quantity of nutrients in the aqueous phase. To assess the feasibility of utilizing the aqueous phase, HTL of *Nannochloropsis* sp. was carried out in the temperature range of 275 to 350 °C and Residence Times (RT) ranging between 5 and 60 min. The effect of reaction conditions on the NO_3^- , PO_4^{3-} , SO_4^{2-} , Cl^- , Na^+ , and K^+ ions as well as Chemical Oxygen Demand (COD) and pH was investigated with view of recycling the aqueous phase for either cultivation or energy generation via Anaerobic Digestion (AD), quantified via Lifecycle Assessment (LCA). In addition to substantial nutrient partitioning at short RT, an increase in alkalinity to almost pH 10 and decrease in COD at longer RT was observed. The LCA investigation found reaction conditions of 275 °C/30 min and 350 °C/10 min to be most suitable for nutrient and energy recovery but both processing routes offer environmental benefit at all reaction conditions, however recycling for cultivation has marginally better environmental credentials compared to AD.

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1. Introduction

It is well established that the nutrients required for algal cultivation incur significant costs and results in equally high environment burdens owing to the energy and resources employed during their synthesis/

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production (Clarens et al., 2010). Nitrogen and Phosphorus based salts in particular are required in large quantities to support algal growth (Clarens et al., 2010; Johnson et al., 2013; Patel et al., 2012), and when implemented at scale, these inorganics may well become a limiting factor, especially considering the impending peak Phosphorus theory suggesting a shortage in coming decades with no real substitute possible (Beardsley, 2011). Even if sea water were used for commercial cultivation, the replenishment of nutrients, such as nitrogen-based ammonium salts, phosphorus and sulphates would still be necessary (Chebil and Yamasaki, 1998). Demirbas (2010) estimated that for commercial production of microalgae, approximately 8 to 15 tons of fertilisers are required per hectare per year. The production of fertilisers is energy intensive and requires substantial resource inputs, which is one of the bottlenecks for achieving a high economic return for mass cultivation of algae to date (Clarens et al., 2010). Consequently, the preparation of growth medium also contributes considerably to the high biofuel production cost (Grima et al., 2003), particularly where a saline growth medium is needed. Most of these nutrients are absorbed by algal cells to synthesise and maintain their chemical composition as well as survive and therefore nutrient reclamation would involve direct removal/extraction from algal biomass, ideally without additional treatment or affecting the product pool.

Amongst various processing technologies for biomass transformation to fuel/chemicals, treatment of wet algae paste under elevated temperature and pressure via Hydrothermal Liquefaction (HTL) is considered to be a promising route, especially since HTL also makes the recovery and recycling of inorganic nutrients possible (Patel et al., 2016; Patel et al., 2014; Peterson et al., 2008). Nutrient recycling is especially important because not all of the input nutrients are consumed completely by algae and some end up in the aqueous phase after HTL. Furthermore, during hydrothermal treatment the inorganics bound to the biomass can be retrieved as it is not desirable to have these in the oil phase, thus alleviating special treatment. Therefore, recycling the nutrient-rich and carbon-containing aqueous phase after HTL could be a solution via nutrient reclamation for algal cultivation, which would help to reduce the input of fertilisers; another potential use is aqueous stream recycling for energy generation via Anaerobic Digestion (AD).

The concept of using HTL produced water for growth has already been demonstrated by Biller et al. (2012) who recycled HTL (at 300 and 350 °C) aqueous phase for cultivation of four algae species, namely *Chlorella vulgaris*, *Scenedesmus dimorphus*, *Spirulina platensis* and *Chlorogloeopsis fritschii*. This study indicated the feasibility of recycling the HTL aqueous phase based on the high concentration of a range of nutrients required for algae growth, and this has been confirmed by other studies which showed successfully cultivated algae using various concentrations of HTL aqueous phase (Alba et al., 2013; Biller et al., 2012 and Nelson et al., 2013). However, the effect of Residence Time (RT) on inorganics concentration in the aqueous phase is unknown. Particularly, recent studies (Faeth et al., 2013, Patel and Hellgardt, 2015 and Patel and Hellgardt, 2013) have suggested that HTL can be carried out at shorter RT and as a result, it is necessary to observe the partitioning of inorganics with respect to RT and to evaluate the feasibility to re-use the aqueous phase obtained at these reaction conditions. An alternative to nutrient reclamation is to digest the carbon-containing aqueous phase and recover energy via AD. However, deciding the most desirable method for HTL aqueous phase recovery should take into account economic and environmental variables. To elucidate the knowledge gap, this study focuses on the environmental aspects, where the holistic environmental impacts of two alternatives for aqueous phase treatment are compared using an LCA approach.

This manuscript investigates the concentration of recoverable nutrients and the potential to re-use/recycle the aqueous phase. Experiments were carried out using a batch reactor to investigate the effects of processing temperatures (275, 300, 325 and 350 °C) and RT(5, 10, 15, 20, 30, 45 and 60 min) on the concentration of sodium, potassium, sulphates, phosphates, nitrates and trace metals in the aqueous phase. In

addition, the experimental data is fed into an LCA model to investigate the environmental impacts for aqueous phase utilisation as cultivation medium and AD feedstock. To our best knowledge, the analysis of inorganics with respect to RT of HTL reaction and subsequent environmental assessment of recovered aqueous phase has not been addressed in any publically available literatures.

2. Experimental

Freeze dried *Nannochloropsis* sp. algae was obtained from the University of Almeria. All chemicals used for standards, sample preparation and extraction protocol were obtained from Sigma Aldrich Ltd. (unless stated otherwise) and used as purchased (purity > 98%). The batch reactors were constructed in-house using Stainless Steel (316 L) tubes and cap endings on either side, purchased from Swagelok®.

2.1. Reaction

The hydrothermal liquefaction of the microalgae was carried out in 1/2 inch outer diameter 316 L stainless steel batch reactors of volume 6 cm³ in an isothermal recirculating oven. To expose the reactors to hydrothermal conditions and condition them, all fabricated reactors were filled with De-Ionised Water (DIW) and placed in the oven for 3 h at 380 °C. In a typical run, a fresh stock supply of 10 wt% algae paste was made and 3 g of this stock solution was added to the reactor and the reactor sealed. It was then placed in the oven at required temperature (275, 300, 325, 350 °C) and removed at designated RT(5, 10, 15, 20, 30, 45, 60 min). The reactor was immediately quenched in ice and left overnight to equilibrate. The mass of reactor (+ contents) before and after the reaction was measured to ensure no leakage occurred during the reaction.

2.2. Product extraction

The quenched batch reactor was slowly opened to release any produced gas and rinsed with Dichloromethane (DCM) to extract the products. A spatula was used to remove char stuck to the reactor walls. The product was left to settle for 2 h to allow the organic rich DCM and aqueous phase to separate. A 2 ml aliquot of the top aqueous phase was taken for analysis and filtered through a 0.22 µm membrane filter. The remaining aqueous phase was stored in a fridge. After allowing the filtrate to separate in a separating funnel, the lower DCM solubilised biocrude phase was filtered, separated and run through anhydrous MgSO₄ column to remove residual water. Moisture free biocrude was obtained by evaporating DCM over a steady stream of Nitrogen at room temperature for 5 h. The pH of the extracted aqueous phase was also measured.

2.3. Feedstock inorganic composition

The initial inorganic (trace metals) composition was determined as follows. A sample of 0.15–0.30 g freeze dried algae was added to a 60 ml Teflon vessel (Saville), with 2 ml of concentrated Nitric Acid at 70 °C for 4 h followed by the addition of 5 ml of concentrated Hydrochloric Acid and left to evaporate for 3 h. The dried sample was then subjected to addition of 1 ml 70% Perchloric Acid at 100 °C and left for 2 h in an open vessel. The vessel was then tightly closed and kept at 130 °C for 48 h. After cooling adding 0.2 ml 40% Hydrofluoric Acid the vessel was placed in an oven at 130 °C for 4 h. The samples were then dried at 150 °C prior to preparation for Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) analysis using 7% Nitric Acid.

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