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Hydrothermal upgrading of algae paste in a continuous flow reactor

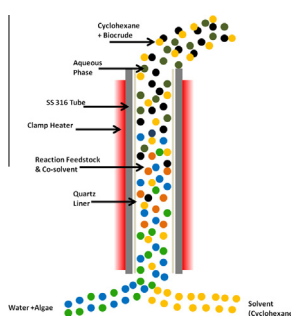
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HIGHLIGHTS

- Continuous HTL of algal biomass in a quartz lined plug flow reactor.
- Production of algal biocrude at short residence time.
- Analysis of biocrude from continuous fast liquefaction.

GRAPHICAL ABSTRACT



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ABSTRACT

This investigation demonstrates the utility of a novel laboratory scale continuous plug flow reactor for fast Hydrothermal Liquefaction (HTL) of microalgae in a quartz lined chamber. Reactions were carried out between 300 and 380 °C and residence times of 0.5–4 min. Cyclohexane was used as a co-solvent to enhance extraction and prevent char formation. Highest biocrude yield of 38 wt.% was achieved at 380 °C and 30 s as well as Water Soluble Fraction containing up to 60 wt.% matter recovered. Analysis of the biocrude showed that the extent of deoxygenation and denitrogenation after HTL varied and is dependent on the reaction conditions. Fourier Transform Infrared Spectroscopy analysis showed that biocrude contains similar functional moieties with only a small difference observed at different reaction conditions. Conversely, the Simulated Distillation and Size Exclusion Chromatography data showed that harsher conditions produced marginally better biocrude with improved boiling point profile and lower molecular weight compounds, respectively which was confirmed using Gas Chromatography–Mass Spectrometry.

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1. Introduction

The rise in global population and improvement in living standards is increasing the world's energy demand. The U.S. Energy Information Administration (EIA) estimates a 56% increase in global energy consumption by 2040 based on 2010 projections of 524 quadrillion Btu (EIA, 2013). Currently the primary source of energy is via combustion of finite fossil fuel resources that has caused considerable increase in atmospheric CO₂ with

unprecedented levels reaching 400 ppm (Ewald, 2013). Utilisation of fuel in the transportation sector is particularly problematic as tailpipe emission accounts for the second highest CO₂ release. An alternative to fossil fuels for transportation is to convert biomass to liquid fuel. Third generation feedstock such as algae has garnered significant interest recently due to its ability to fix carbon rapidly, high productivity and photosynthetic efficiency as well as its cultivation location not requiring agricultural land, thus not competing with food crops (Patel et al., 2012). A promising processing technology used to convert algal biomass to fuel precursors is Hydrothermal Liquefaction (HTL) which entails treatment of algal slurry at elevated temperature and pressure with water.

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Concentrating and drying of algal biomass is associated with severe energy penalty (Patel et al., 2012). Therefore, eliminating the drying process and directly processing concentrated wet algae using HTL is of great interest for conversion of algal biomass to biocrude by merely exploiting the modified properties of water at high temperature and pressure. As water approaches its critical point, the ionic product (K_w) increases, enabling it to act as an acid or base catalyst during reactions. Furthermore, the increase in dielectric constant and decrease in Hildebrand solubility parameter indicate that water can increasingly act as an organic solvent, enhancing solubility of organic molecules (Savage, 1999). The lipid, protein and carbohydrate macromolecules present in algae are susceptible to degradation/cracking and rapid hydrolysis under hydrothermal conditions. Hence, hydrothermal water is well suited for application as a biomass liquefaction medium.

Compared to algal pyrolysis, HTL produces biocrude with better Higher Heating Value (HHV) and also offers the potential to recycle processed water and recover nutrients from the growth medium (López Barreiro et al., 2013). HTL is based on the premise that it is possible to deoxygenate and denitrify biomass, as an initial processing step, without the use of chemicals to produce biocrude. The biocrude produced from HTL has a HHV similar to crude oil (Vardon et al., 2011). Further post processing of biocrude is necessary to either convert it directly to fuel or blending with fossil crude at refineries as demonstrated by Elliott et al. (2013).

HTL has been studied by various researchers (Reddy et al., 2013; Valdez et al., 2012; Vardon et al., 2011, 2012; Garcia Alba et al., 2011; Chen et al., 2014) to produce biocrude with variable properties such as energy content, boiling point distribution, (CHNO) elemental content and product yield using several different species of algae under different reaction conditions (heating rate, volume, water:algae ratio and autogenic pressure). But, the majority of research thus far has focused primarily on the use of batch reactor systems. The outcome of these investigations concluded that liquefaction at low Residence Time (RT) could be suitable to produce algal biocrude (Patel and Hellgardt, 2013; Faeth et al., 2013) since catalytic post processing is always necessary and energy expenditure can be limited by shorter contact time during HTL. However, batch reactors are not entirely suitable for biomass liquefaction at short RT due to the variability in heating rate, heating time, uncertainty in autogenic pressure/mixing and post reaction cooling. It is also clear that at scale, only flow reactors are likely to be implemented. Hence, evidence suggests a gradual shift in the research community moving towards implementation of continuous flow reactors (Elliott et al., 2015).

Jazrawi et al. (2013) and Elliott et al. (2013) have both successfully demonstrated the application of a pilot scale flow reactor system for HTL of *Nannochloropsis* and *Chorella* sp., but the implementation of such system at a much smaller laboratory scale has not yet been attempted for detailed studies of algal HTL.

The aforementioned pilot studies only employed neat water during processing and RTs of minutes. From trials in the laboratory it was found that the HTL flow reactor system was susceptible to solid char deposition (especially post reactor) and potential catalytic wall effects (Maiella and Brill, 1998; Chakinala et al., 2009; Potic et al., 2004) arising from the SS316 material under hydrothermal conditions which could contribute towards the HTL reaction. In addition to the charring, the biocrude yield was also consistently low (approximately 20 wt.% at RT between 1 and 5 min and temperature 300–350 °C) during trials, thus further improvement was necessary.

To address these issues, firstly the reactor wall was lined with an inert quartz liner, and in order to promote reactive extraction and minimise char deposition, a co-solvent namely cyclohexane was fed into the reactor during HTL. From previous work in the laboratory, cyclohexane was found to be rather stable under

hydrothermal conditions. Short to medium chain hydrocarbons (or kerosene) or alcohols could also be used but due to their potential to skew the product mixture during analysis, these were not selected. The outcome from the co-solvent and quartz liner during further trials of the reactor system showed improvement in the biocrude yields confirming adverse effect in the system in their absence.

Thus, based on the above and scoping the literature it can be confirmed that a quartz lined extractive flow reactor at laboratory scale has not been demonstrated previously for algal HTL. This work demonstrates the use of such a system and presents the findings of hydrothermal algal biomass conversion (or hydrolysis) to biocrude under various reaction conditions.

2. Method/experimental

2.1. Flow reactor

The schematic of the in-house constructed reactor is presented in Fig. 1. The quartz liner was enclosed in a 0.95 cm outer diameter SS316 L tube of length 20 cm to give a total reactor volume of 2 cm³. For a typical reaction, the reactor system was first pressurised to 180 bar by a JASCO 780 piston pump and a ISCO 1820 syringe pump to feed DIW (De-Ionised Water) (later algae paste) and cyclohexane, respectively. Consecutively, the reactor heater was set to the required temperature and the pump flow rates adjusted to achieve the desired RT, and maintain a 10 vol.% cyclohexane concentration through the 2 ml reactor. Once the reaction temperature was attained, the system was allowed to stabilise for approximate 5 RT (or 5 × reactor volume) and then the reciprocating High-Performance Liquid Chromatography (HPLC) pump feed switched to pre-prepared algae solution of 1.5 wt.% *Nannochloropsis* sp. biomass concentration. The algal solution feed tank was stirred to prevent the algae from settling. Based on initial trial runs it was confirmed that the reactor takes approximately 5 RT (or 5 reactor volume (10 ml)) to reach steady-state after which sample collection was initiated continuously for the duration of the reaction. Upon pumping 150 ml of algae solution, the reactor heater was switched off and the reactor flushed thoroughly with a total volume of 50 ml DIW and cyclohexane at the reaction flow rate. The 'post reaction' sample of about 50 ml was collected separately whilst the reaction temperature reduced to ambient. The reactor system was further dismantled and the Back Pressure Regulator (BPR) flushed with cyclohexane:water mixture. Only a small quantity of produced residual organic matter was collected upstream to the BPR using this method.

The primary 150 ml solution was then filtered, filter paper rinsed with Dichloromethane (DCM) and the filtrate transferred to a separating funnel to obtain the DCM soluble organic phase from which the solvent was evaporated under a steady stream of nitrogen to obtain the biocrude. Given the low concentration of cyclohexane compared to DCM, both solvents evaporated readily at room temperature within 5 h. The filter paper was allowed to dry and a sample of the retained solids collected and weighed for elemental analysis. The leftover material, classed earlier as 'post reaction' sample was now treated as above. Typically the 'post reaction' organic phase extract contained 10–15 wt.% of the total extracted biocrude.

2.2. Size Exclusion Chromatography (SEC)

SEC was used to determine the approximate molecular weight distribution of produced biocrude. Roughly 10 mg of biocrude was dissolved in 2 ml 1-methyl-2-pyrrolidinone (NMP) and filtered through a 0.45 µm PTFE filter. 10 µl of the sample was injected in a

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