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Hydroprocessing of bio-crude from continuous hydrothermal liquefaction of microalgae

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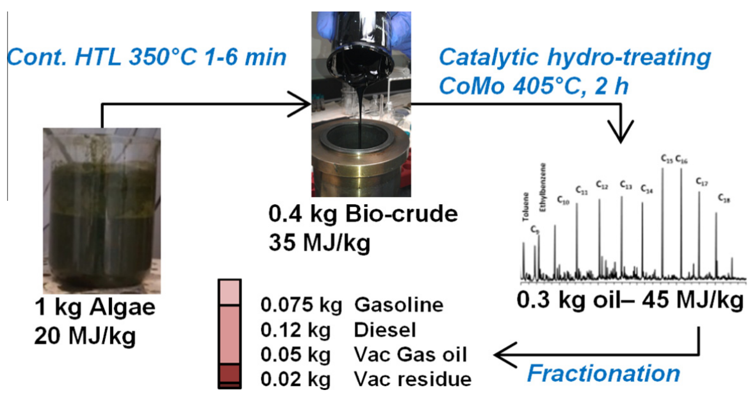
HIGHLIGHTS

- Novel continuous HTL reactor for microalgae is presented.
- Residence times of 1–6 min resulted in up to 40% bio-crude yields.
- Lower residence time resulted in higher O in bio-crude.
- Hydroprocessing of bio-crude results in reduction of N and O.
- Further reduction of O using solvent extraction possible.

GRAPHICAL ABSTRACT



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ABSTRACT

Hydrothermal liquefaction (HTL) has developed as one of the most promising technologies for biofuel production from wet biomass feedstocks in recent years. In the current study, a microalgae slurry was processed in a continuous flow hydrothermal processing unit capable of 2.5 l/h flow rates, temperatures of 350 °C and pressure of up to 206 bar. 40 wt.% bio-crude yields were obtained when processing *Chlorella* at residence times of 1.4 and 5.8 min. The higher heating value of the bio-crude was approximately 35 MJ/kg, however the nitrogen content of 6% and oxygen content of 11% render it unsuitable for direct combustion. In order to investigate the upgrading potential, the bio-crude was hydroprocessed using CoMo and NiMo catalysts at two temperatures (350 °C and 405 °C) in a stirred reactor. Both catalysts showed similar activity during hydroprocessing. Nitrogen content was typically reduced by 60% at 405 °C whereas oxygen content was reduced by 85%. Fractionation of the upgraded oils result in approximately 25% gasoline, 50% diesel and 25% heavy fuel oil fractions. Further analysis of oils by GC–MS, Sim-Dis and elemental analysis give insight into the fuel quality and nitrogen fractionation. The majority of oxygen is shown to be associated with high molecular weight material and can be reduced further following solvent extraction of the oils while the nitrogen content could only be reduced slightly.

1. Introduction

Hydrothermal liquefaction has gained increased interest in recent years as it develops as a promising technology for the production of biofuels from wet organic feedstocks. Microalgae have

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been identified as a particularly suitable feedstock for HTL. Cultivation is performed in aqueous media and minimum energy is required to achieve a feedstock with suitable solids content for processing via HTL [1]. Its high growth rates, lipid contents and non-competition with arable land are advantageous over terrestrial biomass [2]. Research and development in HTL is typically performed at 10–20 wt.% solids in water, temperatures of around 300–350 °C, pressure above the saturation pressure of water and residence times of up to 60 min in batch reactors. This type of research has received tremendous attention in recent years with investigations into different types of algae and varying operating conditions [3–6], various review papers have summarised the research on HTL of microalgae [7–9]. More recently, techno-economic analyses and life cycle assessments have been carried out [10–13]. They show that HTL has a better energy return on investment, lower GHG emission and higher economic potential compared to traditional lipid extraction and transesterification technologies from microalgae. Despite the continuing research efforts, there are still some significant bottlenecks concerning the technology. Although the energy recovery in the primary product bio-crude is high, the quality of bio-crude is still an issue. It contains around 5 wt.% nitrogen, 10 wt.% oxygen and exhibits a high viscosity at room temperature. Researchers have investigated the use of heterogeneous and homogeneous catalysts in-situ to achieve improved bio-crude quality [14,15]. Reductions in oxygen, increased yields and higher energy recoveries were obtained, however particularly the reductions in N were only small. Attention has therefore shifted towards the upgrading of the bio-crude using either catalytic hydrotreating and catalytic hydrothermal treatment [16–19]. Bai et al. investigated the use of 15 different catalysts to upgrade bio-crude via catalytic hydrothermal processing in batch reactors in a H_2 atmosphere [20]. They were able to recover 55–77% upgraded fuel with reductions of O and N in the oils. There are only limited studies on the catalytic hydrotreating of bio-crude without water being present [16,21]. Elliott et al. hydrotreated the bio-crude from continuous HTL using CoMo catalysts in a trickle bed reactor, achieving approximately 80% upgraded oil yield and final O and N levels of ~1 and ~0.1 wt.% respectively. Hydroprocessing of bio-oils from pyrolysis and HTL has been reviewed by Elliott [22]. It has also been suggested that the H_2 required for hydrotreating of bio-crudes can be obtained via catalytic hydrothermal gasification of the organic rich aqueous phase from HTL [23]. This would improve the carbon efficiency and economics of the process while still recovering nutrients such as N and P for the cultivation of algae. The concept of recycling nutrients has successfully been demonstrated on a variety of microalgae strains in batch processes [24–26].

The other bottleneck concerning HTL of microalgae is the lack of continuous processing data. In order to achieve significant scale and market competitiveness, continuous processing is necessary. There are currently only two groups with publications of continuous hydrothermal liquefaction of microalgae [21,27]. Researchers at the Pacific Northwest National Laboratories (PNNL) processed four different microalgae slurries in a continuous flow reactor at ~350 °C and residence times of ~25 to 40 min, leading to bio-crude yields of up to 64 wt.%. Recently Savage's research group was able to show that very low residence times and high heating rates in batch reactors can lead to higher yields and energy recoveries in the bio-crude [28]. These results were confirmed by the work of Jazrawi et al. who processed *Chlorella* and *Spirulina* at residence time of 3–8 min in a continuous HTL reactor and achieved bio-crude yields of up to 42 wt.% [27]. These lower residences times allow for higher throughput and reduced energy consumption in continuous systems. Continuous hydrothermal liquefaction of biomass has recently been reviewed by Elliott et al. [23]; the review shows the distinct lack of reports in the literature on continuous HTL of microalgae.

In the current investigation results are presented for the processing of a low lipid microalgae *Chlorella* on a custom built continuous reactor system. The bio-crude is upgraded via hydrotreatment using either no catalyst or NiMo and CoMo catalysts at two different temperatures. The performance of the continuous hydrothermal reactor is discussed. Comprehensive analysis is carried out on the bio-crude and upgraded fuel to investigate its fuel properties and the fate of nitrogen and oxygen following hydrotreatment. This investigation is the first to study fast heating rate, low residence time continuous HTL of microalgae and subsequent upgrading of bio-crude to a refinery ready feedstock. Further novel results and discussion is presented on the high molecular weight fraction of bio-crudes and upgraded oils using pyrolysis gas-chromatography mass-spectrometry (Py-GC–MS) to elucidate the fate of nitrogen and oxygen during continuous HTL and hydroprocessing.

2. Materials and methods

Chlorella (cell walls intact, 80–120 mesh) microalgae was obtained from Sunrise Nutrachem Group, Qingdao Sunrise Trading Co., Ltd. (China). Experimental procedures for the determination of ash, moisture, CHNSO content and biochemical composition were determined as described previously [29]. Cobalt molybdenum and nickel molybdenum on alumina catalysts (1–2 mm size) were provided by Johnson Matthey (London, UK). Chemicals and reagents were obtained from Sigma–Aldrich (dichloromethane, kerosene, dimethyldisulfide, tetrahydrofuran (THF), pentane).

The continuous HTL reactor was custom built at the University of Leeds. Its schematic layout is presented in Fig. 1. All piping is made of 316 SS Swagelok 0.6335 mm outer diameter, 0.0899 mm wall thickness tubes. The reactor is submerged into a FSB 3 Fluidised Sand Bath (Omega Engineering, USA). The reactor is made of 4 coils of 1.5 m length (98 mL total volume) connected in series and fully submerged in hot fluidised sand. The microalgae feed slurry was prepared by mixing 10 wt.% dry *Chlorella* microalgae with distilled water using a domestic food mixer. The slurry was kept in a pre-mixed beaker using a magnetic stirrer to obtain uniform solids concentrations throughout the experimental runs. A head pressure of 0.06 bar from the mixing chamber to the pump was sufficient to provide feed for the high pressure pump. A Series 900 hydraulic diaphragm metering pump from Aquflow (Irvine, CA, USA) was used to pump the slurry and obtain the required pressure

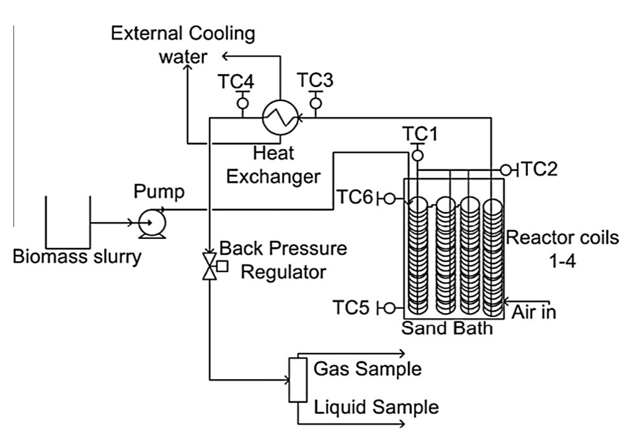

Fig. 1. Schematic layout of the continuous HTL reactor.