



# Hydrogen production from the catalytic supercritical water gasification of process water generated from hydrothermal liquefaction of microalgae



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## ABSTRACT

The integration of hydrothermal liquefaction (HTL) and hydrothermal gasification (HTG) is an option for enhanced energy recovery and potential biocrude upgrading. The yields and product distribution obtained from the HTL of *Chlorella vulgaris* have been investigated. High conversion of algae to biocrude as well as near complete gasification of the remaining organic components in the aqueous phase was achieved. The aqueous phase from HTL was upgraded through catalytic HTG under supercritical water conditions to maximise hydrogen production for biocrude hydrotreating. High yields of hydrogen were produced (~30 mol H<sub>2</sub>/kg algae) with near complete gasification of the organics (~98%). The amount of hydrogen produced was compared to the amounts needed for complete hydrotreating of the biocrude. A maximum of 0.29 g H<sub>2</sub> was produced through HTG per gram of biocrude produced by HTL. The nutrient content of the aqueous phase was analysed to determine suitability of nutrient recovery for algal growth. The results indicate the successful integration of HTL and HTG to produce excess hydrogen and maintain nutrient recovery for algal growth.

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## 1. Introduction

Algal biomass is a promising feedstock for renewable fuels due to its high photosynthetic efficiency resulting in high growth rates and improved CO<sub>2</sub> mitigation [1,2]. The main focus has been on the extraction of fatty acids and triglycerides and subsequent transesterification for biodiesel production [3,4]. The main challenge lies in the fact that most common lipid extraction techniques require a dry feedstock before transesterification. Obtaining a dry feedstock can incur an energy penalty accounting for as much as 25% of the energy contained in the algae [5]. An alternative option is the wet processing of the whole algae, thus including the carbohydrates and proteins. One such wet processing route is hydrothermal liquefaction (HTL) where the wet feedstock is processed at high temperatures (250–350 °C) and pressures (5–24 MPa) with or without catalysts to produce an upgradable biocrude fraction, as well as water, gaseous and solid fractions. During HTL, the feedstock is hydrolysed into smaller reactive molecules which repolymerise to form oil compounds [6].

Batch HTL studies have received the greater share of the research focus with product recovery by solvent extraction. Typical

batch HTL experiments have been conducted on microalgae with different biochemical content resulting in biocrude yields of around 25–40 wt% (daf) with higher heating values (HHV) of 30–35 MJ/kg [7–11]. Biocrude yields have been reported at 10–15% higher than the lipid content of the algae proving that part of the oil is derived from the carbohydrate and protein fractions. This has been demonstrated for both high lipid microalgae [9,12] and low lipid microalgae [13,14]. For a review on the developments from batch to continuous processes for the HTL of biomass (including algae), see Elliott et al. [15].

Biocrude from algal HTL tends to be viscous and tar-like with a significant amount of heteroatoms – oxygen, nitrogen and sulphur. Therefore, it is not directly suitable for storage, transport and use as a transport fuel. Attempts at catalysing the HTL process to improve the quality of the biocrude produced involved the use of alkali (Na<sub>2</sub>CO<sub>3</sub> and KOH) and organic acids (formic and acetic) [7,13]. Results indicated that the use of organic acids improved the flow properties of the biocrude and lowered its boiling point. However, Duan and Savage [16] point out that their studies on catalytic HTL of microalgae suggest that the quality of the biocrude is largely insensitive to the presence or identity of a catalyst and as such, separate upgrading of the biocrude through hydrotreating might be more suitable.

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Hydrotreating involves processing the algal biocrude with hydrogen over a catalyst. Hydrogenation reactions convert oxygen, nitrogen and sulphur to H<sub>2</sub>O, NH<sub>3</sub> and H<sub>2</sub>S respectively. The amount of hydrogen required for hydrotreating depends on the amount of oxygen, nitrogen and sulphur in the biocrude. Frank et al. [17] resorted to a stoichiometric calculation to calculate the hydrogen demand for hydrotreating and calculated a hydrogen demand of 0.023–0.060 g H<sub>2</sub>/g biocrude based on HTL biocrude containing 71% C, 9.2% H, 11% O and 5.7% N.

Jones et al. [18] reported biocrude yields from the continuous HTL of *Nannochloropsis* and *Chlorella* consisting of C (77%), H (9–10%), O (6–8%), N (4–6%), S (0.3–0.7%). These were investigated for hydrotreating and required 0.0375–0.043 g H<sub>2</sub>/g biocrude.

The parameters used in the base case of a life cycle assessment of bio-jet fuel from HTL of microalgae [19] included a minimum value of 0.0235 g H<sub>2</sub>/g feed and a maximum value of 0.0399 g H<sub>2</sub>/g feed. The parameters altered for the optimised case included a hydrogen consumption of 0.0276 g H<sub>2</sub>/g feed as a nominal value. These were calculated based on the conversion of an algal biocrude with a similar elemental composition content to those reported by Jones et al. [18].

The aqueous fraction from algal HTL is often rich in organic carbon and nitrogen and successful recovery is important for their nutrient and economic value. The aqueous fraction ranges between 30% and 50% of the product composition, and can be as high as 68% as demonstrated in the HTL of *Spirulina* [20]. Due to the high nitrogen content, this fraction has a carbon to nitrogen ratio that makes it unsuitable for anaerobic digestion [21]. Therefore, unless the nitrogen content is reduced by precipitation for example [22], anaerobic digestion is being replaced by catalytic hydrothermal gasification as an alternative process in pathway models for life cycle assessments of algal HTL [15,17]. In a recent study on process development for algal HTL in a continuous-flow reactor, Elliott et al. [23], hydrothermally gasified the aqueous phase in the presence of ruthenium catalyst to produce a biogas (~60% CH<sub>4</sub>, 30% CO<sub>2</sub>, 5% NH<sub>3</sub>, and 2% H<sub>2</sub>). The chemical oxygen demand of the water was reduced by 98.8–99.8%. Alternatively, the aqueous organic carbon can be used to produce hydrogen via catalytic hydrothermal gasification with the potential of using the hydrogen for upgrading or partial upgrading of the biocrude [17,24].

In terms of hydrotreating the algal HTL biocrude, Jones et al. [18] discuss that the biocrude would ideally be transported to a centralised upgrader that accepts oil/biocrude from multiple sites to realise commercial economies of scale. However, initial upgrading may be required to process the algal biocrude to achieve oxygen, nitrogen and sulphur levels that could be tolerated in a conventional plant.

This study investigates the supercritical water gasification of the aqueous phase of microalgal HTL to maximise hydrogen production for biocrude hydrotreating. During hydrothermal gasification, water above its critical point (>374 °C and >22.1 MPa), acts as a non-polar organic solvent with high diffusivity and low dielectric constant. These properties ensure fast reaction rates and high mass transfer rates for organic chemical reactions such as gasification. Using the water content of the aqueous fractions from microalgae liquefaction as the reaction medium to convert its organic contents to hydrogen for hydrotreating biocrude would promote energy recovery and process economics.

Following HTL of *Chlorella*, the amount of hydrogen produced from SCWG of the HTL aqueous phase is compared to the amounts needed for complete hydrotreating of the algal biocrude. In addition, the nutrient content of the aqueous phase post gasification is studied to assess the potential for nutrient recycling for algal cultivation. *Chlorella* was initially tested at varying hold times to study the effect on biocrude quality and organic content of the aqueous phase.

## 2. Experimental

### 2.1. Materials

Samples of *Chlorella vulgaris* were obtained from Sunrise Nutrachem Group, Qingdao Sunrise Trading Co., Ltd. (China). The proximate and ultimate analysis of the microalgae including the biochemical composition is listed in Table 1. The C, H, N, and S content of the sample was measured using a CE Instruments Flash EA 1112 series elemental analyser. The measurements were repeated in duplicate and a mean value is reported. The higher heating value (HHV) of the sample was calculated according to the equation proposed by Channiwal and Parikh [25] based on the sample's elemental composition:

$$\text{HHV} = (349.1\text{C} + 1178.3\text{H} + 100.5\text{S} - 103.4\text{O} - 15.1\text{N} - 21.1\text{ASH})/1000 \text{ MJ/kg}$$

Sodium hydroxide pellets were obtained from Sigma-Aldrich UK and used as gasification additive.

### 2.2. Experimental procedure

Hydrothermal liquefaction experiments were performed in a non-stirred batch stainless steel Parr reactor with a volume capacity of 500 ml, designed to a maximum temperature and pressure of 500 °C and 35 MPa. The reactor was heated by a 3 kW ceramic heater. The reactor was loaded with 6 g of the microalgae mixed with 60 ml of deionised water as a pre-mixed slurry. The reactor was purged with nitrogen and heated from ambient pressure at an average rate of 10 °C/min to 350 °C and held for the designated reaction time (0, 30, 60 min; with 0 min indicating that the reaction is quenched once the reactor reaches the target temperature of 350 °C). At the end of each experiment, the reactor was rapidly cooled using compressed air and the final pressure noted once the reactor reached room temperature.

Following liquefaction, the gas fraction was sampled and analysed offline through gas chromatography. 100 ml of dichloromethane was added to the reaction mixture and the contents separated without the addition of any water (to avoid diluting the aqueous phase). The solvent was removed by evaporation to determine the mass of the biocrude. The biocrude yield is determined using Eq. (1).

$$\text{Yield} = \frac{\text{Biocrude mass}}{\text{Algae mass} \times (100 - \text{H}_2\text{O} - \text{Ash})/100} \quad (1)$$

The C, H, N, S content of the biocrude was measured using a CE Instruments Flash EA 1112 series elemental analyser. All measurements were repeated in duplicate and a mean value reported.

Supercritical water gasification (SCWG) experiments were performed in a batch Inconel reactor (75 ml, Parr, USA). Details of the reactor have been provided in previous publications [26,27]. Briefly, the reactor has a 75 ml volume capacity and is rated to 600 °C and 35 MPa. The reactor was heated by a 1.5 kW ceramic knuckle heater and the reactor temperature was monitored by J-type thermocouple held in a thermowell at the bottom of the

**Table 1**

Proximate, ultimate analysis and biochemical composition of the feedstock investigated.

| Sample name | Proximate (%) |      | Ultimate (% daf) |     |     |     | HHV (MJ/kg) |                |
|-------------|---------------|------|------------------|-----|-----|-----|-------------|----------------|
|             | Moisture      | Ash  | C                | H   | N   | S   |             | O <sup>a</sup> |
| Chlorella   | 5.20          | 6.40 | 53.6             | 7.3 | 9.2 | 0.5 | 29.4        | 24.0           |

<sup>a</sup> By difference, daf: dry ash free.

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