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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_2/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_2 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_2 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_2CO_3 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_2O, NH_3 and H_2S 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_2/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_2/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_2/g feed and a maximum value of 0.0399 g H_2/g feed. The parameters altered for the optimised case included a hydrogen consumption of 0.0276 g H_2/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_4, 30% CO_2, 5% NH_3, and 2% H_2). 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 Channiwala and Parikh [25] based on the sample's elemental composition:

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

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).

$$\mathrm{Yield} = \frac{\text{Biocrude mass}}{\text{Algae mass} \times (100 - \mathrm{H_2O} - \mathrm{Ash})/100} \quad (1)$$

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[a]	
Chlorella	5.20	6.40	53.6	7.3	9.2	0.5	29.4	24.0

[a] By difference, daf: dry ash free.

reactor. The operating pressure was measured with a pressure gauge mounted on the reactor head. Each experiment involved loading the reactor with 15 ml of the diluted or undiluted aqueous phase from the HTL experiment to reflect the required concentration to be gasified. The reactor was purged with nitrogen and heated at an average rate of 30 °C/min to the required temperature and held for 30 min. At the end of each test, the reactor was rapidly cooled using compressed air and the final pressure noted once the reactor reached room temperature. The product gas was sampled for offline gas chromatography analysis by taking two 30 ml gas samples to allow for reproducible gas analysis from each experiment.

The HTL and HTG of Chlorella at 0 min hold time was repeated in triplicate to determine variability in the product yields (including gas analysis). The resulting product yields and gas analysis showed a standard variation of <5%. In addition, several results have been published using the same batch reactor with good reproducibility [28,29]. Gas analysis from HTL and HTG experiments were performed in duplicate and a mean value reported. The post gasification aqueous fraction (HTG water) was transferred from the reactor and analysed for organic carbon and nutrient content by ion chromatography. The TOC content of the aqueous phase was determined in triplicate and a mean value reported and the nutrient content by ion chromatography was determined in duplicate and a mean value reported.

2.3. Analysis of products

2.3.1. Gas analysis

Hydrocarbon gases including methane and C_2–C_4 gases were analysed using a gas chromatograph fitted with a flame ionisation detector (Varian C-3380 GC/FID). The column was 2 m long by 2 mm diameter and packed with 80–100 mesh Hysesp. Hydrogen, carbon monoxide and carbon dioxide were analysed by separate gas chromatographs fitted with thermal conductivity detectors. A 2 m long by 2 mm diameter, 60–80 mesh packed molecular sieve column was used to separate hydrogen, oxygen, nitrogen and carbon monoxide. A packed Hysesp column of similar dimensions was used for carbon dioxide analysis. Results were obtained in volume percent, converted to moles using the ideal gas law, from which the mass of each gas product was obtained.

2.3.2. HTL and HTG process water analyses

Samples of the aqueous fractions from HTL and HTG were diluted to a known volume and analysed for total organic carbon content by a TOC analyser (HACH IL 550 TOC-TN). The main anions and cations were identified and quantified by ion chromatography (DX-100, Dionex, USA).

3. Results and discussion

3.1. Hydrothermal liquefaction (HTL) at varying hold times

The distribution of products from the HTL of *Chlorella*, at 350 °C for 0, 30 and 60 min is shown in Fig. 1. A slight increase in biocrude yield was observed as the holding time increased. The increase in biocrude yield was very small; approximately, 1% from 0 to 30 min and 3% from 30 to 60 min. More pronounced variations in biocrude yield is observed when varying the holding time at much lower HTL temperatures of around 175–275 °C [6]. An increase in total organic carbon (TOC) in the aqueous phase was also observed as the holding time increased. There was a significant increase (~55%) in TOC when the holding time was increased from 0 to 30 min with only small increases in TOC content of the aqueous phase when increasing the holding time to 60 min.

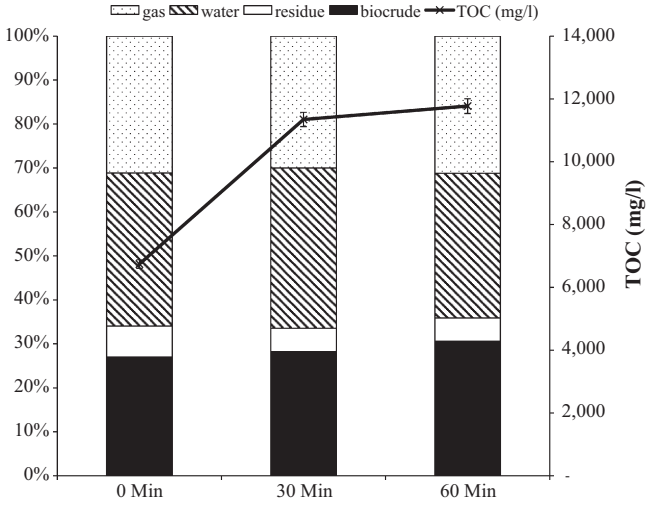

Fig. 1. Product distribution from the HTL of *Chlorella* at 350 °C at varying hold time.

HTL of *Chlorella* at 0 min holding time was repeated and the oil extracted without the use of a solvent to study the effects on the organic carbon content of the aqueous phase and the quality of the biocrude. A breakdown of the products of HTL of *Chlorella* at 0 min without the use of solvent was not presented due to the difficulty in extracting all the biocrude on the reactor walls without the use of a solvent. The TOC content of the aqueous phase using no solvent (13,000 mg/l) was approximately double that of the aqueous phase when solvent was used (7000 mg/l) to extract the biocrude suggesting that the solvent extracts a large amount of organic carbon dissolved in the aqueous phase. The ultimate analysis of the biocrude is presented in Table 2. The main difference between the quality of the biocrude extracted with a solvent is the nitrogen content (6.1%) compared to the biocrude separated without solvent (5.3%). Similar results have been reported in terms of lower nitrogen content in the biocrude without solvent extraction and explained by the higher content of cyclic N-containing compounds in the biocrude extracted with a solvent [30].

Comparing the biocrude extracted with a solvent at varying hold times, the carbon content of the biocrude increased and the nitrogen and oxygen content decreased with increasing holding time. In addition, an increase in hold time from 0 min to 30 min resulted in a decrease in the TOC content of the aqueous phase by 17%. This indicates that increasing the hold time promotes oil forming reactions converting water soluble products into oil – an observation also noted by Garcia Alba et al. in studying the effect of hold time and temperature on the HTL of microalgae [6]. In addition, oil deoxygenation and denitrogenation were achieved as the hold time increased.

A breakdown of the gas products from the HTL of *Chlorella* at varying hold times is presented in Table 3. The major constituent of the gas phase is CO_2, approximately 90%. Hydrogen and methane concentrations increased three fold and two fold respectively as

Table 2
Influence of hold time on the biocrude composition from the HTL of *Chlorella* at 350 °C.

Hold time	C (%)	H (%)	N (%)	S (%)	O[a] (%)
0 min (no solvent)	73.2	8.5	5.3	0.7	12.3
0 min	73.2	9.0	6.1	0.5	11.2
30 min	75.1	9.0	5.2	0.6	10.1
60 min	76.7	9.2	5.0	0.8	8.3

[a] By difference.

Table 3
Influence of hold time on the gas composition from the HTL of *Chlorella* at 350 °C.

Hold time (min)	H_2 (mol/kg)	CH_4 (mol/kg)	CO (mol/kg)	CO_2 (mol/kg)	C_2–C_4 (mol/kg)
0	0.03	0.04	0.31	5.38	0.31
30	0.06	0.05	0.72	5.20	0.35
60	0.10	0.08	0.00	5.54	0.35

Table 4
Gas yields (mol/kg *Chlorella* processed) and gasification efficiency from the SCWG of the aqueous phase from HTL of *Chlorella*.

Concentration (organic loading) (mg/l)	Gas composition (mol/kg)					g H_2/g biocrude	Gasification efficiency (%)
	H_2	CH_4	CO	CO_2	C_2–C_4		
11,000	3.31	1.79	0.25	2.66	0.79	0.021	51.9
11,000 (+1.5 M NaOH)	7.45	2.45	0.00	0.02	0.56	0.048	78.5
2000	23.65	1.65	1.79	11.77	4.64	0.153	94.2
2000 (+1.5 M NaOH)	45.28	1.88	0.00	0.00	5.67	0.292	98.7

Table 5
Nutrients and important metals in ppm from the process waters following HTL Chlorella at varying hold time and SCWG of the HTL aqueous phase at 30 min at different organic loading.

(ppm)	HTL				HTG of HTL 30 min aqueous phase				BBM
	0 min (no solvent)	0 min	30 min	60 min	11,000 mg/l	11,000 mg/l (+1.5 M NaOH)	2000 mg/l	2000 mg/l (+1.5 M NaOH)	
pH	8.2	8.4	8.0	8.6	9.3	12.6	9.34	13.0	
TOC	13,091	6996	10,843	11,771	5219	2327	104	24	
Acetate	9454	6546	8600	8733	4290	2866	1269	1335	
Nitrate	18.2	17.6	18.0	18.6	18.4	17.4			182
Phosphate	8022	3954	3877	4235	3230	969	1715	155	153
Sulphate	560	131	424	392	453	604	32	226	
Ammonium	11,931	10,767	12,339	13,620	10,336	9918	1593		
Potassium	573	438	511	573	491	531	85	308	84
Calcium	27	25	16	13	16	9	12	7	
Magnesium	18.2	16.2	17.2	21	9.6	7.6	2.4	4.4	

the holding times increased from 0 to 60 min. The increase in the yields of hydrogen and methane with longer residence time maybe due to water gas shift and methanation reactions although the concentration of these gases are still very low.

3.2. Hydrothermal gasification of aqueous phase of HTL

Samples of the aqueous phase from the HTL of *Chlorella* at 30 min were gasified under supercritical conditions at varying concentrations. Table 4 presents the gas yields from the supercritical water gasification (SCWG) of the undiluted aqueous phase (11,000 mg TOC/l) and a diluted loading (2000 mg TOC/l) both with and without a catalyst (NaOH). The gas yields presented are those considering the total aqueous phase from the HTL of *Chlorella* at 30 min was gasified at similar loading. The results indicate that a lower organic loading results in a higher gasification efficiency and a higher hydrogen concentrations. Lu et al. [31] reported similar results in studying the effects of solution concentration in the production of hydrogen from biomass gasification in supercritical water. A decrease in the TOC contents from 11,000 mg/l to 2000 mg/l saw the yield of hydrogen increase seven fold. The addition of 1.5 M NaOH to the reaction resulted in a doubling of the hydrogen yield at the same organic loading. This can be attributed to the role of sodium hydroxide in capturing the CO_2 and catalysing the water–gas shift reaction and increasing hydrogen production [28]. The gasification efficiency increased to 94.2% when the organic loading was reduced to 2000 mg/l and a further increase to 98.7% was observed with the addition of sodium hydroxide.

The mass of hydrogen required for hydrotreating the biocrude averages 0.05 g H_2/g biocrude based on the studies reported previously. The mass of hydrogen produced from the SCWG of the aqueous phase is compared with the mass of biocrude produced from HTL of *Chlorella* at 30 min hold time (g H_2/g biocrude column in Table 4). Without diluting the aqueous phase to avoid an energy penalty of gasifying more water, sodium hydroxide must be used to produce enough hydrogen to consider hydrotreating the biocrude. SCWG following dilution of the aqueous phase to 2000 mg/l results in 23.7 mol H_2 per kg *Chlorella* processed and 45.3 mol/kg *Chlorella* processed with the addition of 1.5 M NaOH. This equates to 0.15 g H_2/g and 0.29 g H_2/g biocrude respectively; yields of hydrogen in excess of the requirement for complete hydrotreating of the biocrude. The experiments described in this study are performed in batch reactors. In a continuous system, operating parameters would differ due to faster heating and cooling rates and shorter residence time however the results of these batch experiments demonstrate the potential for providing sufficient hydrogen for upgrading the biocrude using the organic carbon dissolved in the aqueous phase.

3.3. Composition of the aqueous phase

Table 5 lists the main components identified in the aqueous phase from HTL of *Chlorella* at varying hold times and in the aqueous phase from the SCWG of the HTL aqueous phase at different organic loading. Comparing the two experiments at 0 min holding time, the dissolved organic material remains in the aqueous phase

when no solvent is used for biocrude extraction resulting in higher concentrations of acetate and TOC. In addition, the concentration of phosphate is twofold higher when no solvent is used. This may be due to the presence of organophosphates such as phospholipids which are extracted into the solvent during solvent extraction.

A reduction in the concentration of acetate and TOC is observed following SCWG of the HTL aqueous phase. However, no significant change is observed in the concentrations of ammonium, potassium and nitrate following SCWG. The results indicate that the post-SCWG aqueous phases are still rich in nutrients that can be recycled for algal cultivation.

The results are compared to the standard growth medium – BBM. In the HTL aqueous phase, concentrations of phosphate and potassium are orders of magnitude higher than those found in the standard growth medium. These nutrients are important for algal growth and recycling helps ease the economic constraint in algal cultivation. Acetate can act as a substrate for mixotrophic growth, increasing productivity and recycling carbon [32].

4. Conclusions

The aqueous phase from the hydrothermal liquefaction of *Chlorella* is rich in organic carbon that can be hydrothermally gasified under supercritical conditions to optimise hydrogen production. With the addition of sodium hydroxide during gasification, 0.05 g H_2 can be produced from the aqueous phase for every gram of biocrude produced during liquefaction of *Chlorella*. Reducing the concentration of the aqueous phase pre gasification results in higher hydrogen yields; 0.15 g H_2 per gram of biocrude and 0.29 g H_2 with the addition of sodium hydroxide. The aqueous phase post SCWG is still rich in nutrients that can be recycled for algal growth.

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