Pilot Plant Testing of Continuous Hydrothermal Liquefaction of Microalgae

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ABSTRACT

We describe a pilot plant for continuous hydrothermal processing of biomass. Results were obtained for two microalgae strains, Chlorella and Spirulina, across a range of biomass loadings (1-10 wt%), temperatures (250-350 °C), residence times (3-5 minutes) and pressures (150-200 bar). Overall, the bio-crude yields were found to increase with higher biomass loading, higher temperature and longer residence time. More severe reaction conditions also reduced the oxygen content of the bio-crude, while the nitrogen content was found to increase with higher temperatures, indicating an increase in the bio-crude production from the protein fraction of the algae. The maximum bio-crude yield obtained was 41.7 wt% for processing Chlorella with a solids loading of 10 wt% at 350 °C and 3 minutes residence time. The present results suggest maximal yields may be obtained in much shorter residence times under continuous flow hydrothermal processing than batch studies have suggested. The maximal yield, however, may not be optimal in terms of properties.

A substantial fraction of the feedstock carbon reported to the aqueous phase – this was up to 60% but decreased to 30% at the highest biomass loadings. Gas production (>90 mol% CO_2) increased with severity of processing, reaching up to 5% of the feedstock carbon. Finally, the solid yields consistently decreased with increasing temperatures and residence times.

Keywords: hydrothermal upgrading, bio-crude, process scaling.

1 Introduction

In the search for renewable liquid fuels and chemicals, hydrothermal liquefaction (HTL) has been identified as a promising route [1, 2]. During subcritical HTL, biomass is processed as a slurry in hot compressed water at around 200-350 °C and up to 250 bar. Due to the high pressure, the water remains in the liquid state. At these conditions, the dielectric constant is increased and the density is decreased, relative to water at normal temperature and pressure, resulting in hydrocarbons becoming more water-soluble [1]. These conditions allow complex reaction cascades to take place, which include a series of decomposition and repolymerisation reactions resulting in the formation of a bio-crude.

Most of the research on HTL has been carried out in batch reactors [2]. However, continuous operation is required in order to make the bio-crude production process more economically feasible and chemically controllable. Heat recovery from a continuous process enhances the overall energy efficiency. Some researchers have studied HTL on continuous or semi-continuous reaction systems for simple water-soluble monosaccharide model compounds such as glucose [3, 4]. However, only a small number of reports on continuous HTL of biomass reaction systems have been published – these reports deal with waste and lignocellulosic feedstocks and do not include aquatic biomass. Hammerschmidt et al. [5] investigated the hydrothermal processing of food sludge feedstocks with solid concentrations of 6.5, 7.7 and 12 wt%. Homogeneous potassium carbonate and heterogeneous zirconium oxide catalysts were used at processing temperatures of up to 350 °C and residence times of 5-10 minutes in a 0.1L continuous reactor. Makishima et al. [6] investigated the hemicellulose fraction recovered from corn cob in a continuous HTL reactor at 200 °C for 10 minutes, up to 15 wt% solid concentration. Ocfemia et al. [7] processed swine manure in a continuous HTL reactor with a throughput of 48 kg manure slurry per day. At a processing temperature of 305 °C and a residence time of 80 minutes, a bio-oil with a Higher Heating Value (HHV) of 31 MJ/kg could be produced. The reactor was successfully operated for 16 hours continuously.

Due to the high moisture content of microalgae when harvested, HTL is an ideal conversion route as the feedstock does not require drying prior to processing. Additionally, the bio-crude can be formed not only from the lipid content of the feedstock, but also from the carbohydrate and protein fractions of the algae leading to higher overall yields [8]. Batch HTL of microalgae is relatively well-studied and has received increased interest in recent years. Most studies use small 10-1000 ml batch reaction vessels with slow heating rates and long residence times (~1 hour). The results show that a high quality bio-crude suitable for further refining can be produced with properties approximating those of a petroleum crude oil [8-11]. Typically, bio-crude yields of around 30 wt% (daf) are obtained with HHVs of 30-35 MJ/kg. Typical slurry solid concentrations of the batch experiments carried out on microalgae vary from 5-50 wt%. On the one hand, it is generally desirable to increase the solids content in order to be able to process more biomass in a given volume and to minimise the energy required to preheat the process water for a given amount of biomass; on the other hand, achieving a high solids loading itself requires increasing amounts of energy for dewatering and affects the pumpability of the cold slurry. The optimum slurry loading for continuous processing is unknown at this point – it is likely to depend on the biomass itself, its size and rheological properties, as well as on the process configuration and plant hardware.

One of the issues associated with HTL is the large amount of carbon found in the process water. Bhatnagar et al. [12] have suggested that this can be used as a substrate for mixotrophic growth by using the process water to recycle nutrients back for algae cultivation. The proof of concept for combining algae cultivation with the HTL process water was demonstrated by Jena et al. [13] and Biller et al. [14]. This would make the HTL process more viable and improve the life cycle analysis (LCA).

The aim of the current study is to demonstrate, at pilot scale, the technical feasibility of continuous HTL processing of microalgae. Two strains of microalgae were studied in steady flow under a range of conditions and we discuss the process performance and products.

2 Materials and Methods

Algal liquefaction was investigated across a range of conditions including solids loading (1-10 wt%), temperature (250-350 °C) and residence time (3-5 minutes) at constant pressure (150-200 bar).

The microalgae investigated were purchased from Synergy Natural Limited, Australia. Synergy algae are grown in freshwater ponds and are freeze-dried. The biochemical composition is quoted from the supplier. The elemental composition was analysed using a CE instruments Flash EA 1112 Organic Elemental analyser (CE Instruments, UK) to determine the C, H, N, and S content of the microalgae and is reported on a dry ash free basis, with O determined by difference.

The metal content of the algae was determined by digesting 200 mg in 10 ml of HNO_3 in a closed vessel, the digested solution was diluted to 100 ml in distilled water followed by analysis on an Optima 5300 DV inductively coupled plasma spectrometer (ICP) with optical emission spectrometry (Perkin Elmer, Cambridge, UK). The particle size distribution of the dry algae cells was also measured using a Malvern Mastersizer S analyser series 2600 (Malvern Instruments, UK).

To determine the amount of ash and moisture contained in a sample, proximate analysis was carried out. Water content determination was performed in an oven at 105 °C for 2 hours; approximately 3 g of algae sample was weighed in a ceramic crucible and the moisture content determined by weighing the dried biomass. Similarly, in order to measure the amount of total organic material in the biomass samples, the ash content was determined by heating approximately 3 g of dry sample in a muffle furnace for 3 hours at 550 °C.

Proximate and elemental analyses were carried out in duplicate for each sample, with a maximum deviation ±0.3%. Only average values are reported.

A known slurry concentration was prepared by mixing the dried microalgae with 50 litres of distilled water. The slurry viscosity was measured using an automated Anton Parr SVM 3000 viscometer (Anton Parr GmbH, Austria). The algal feedstock solution was processed in the continuous flow pilot plant at the University of Sydney – for each individual run, 2 product samples were collected. Most runs were themselves duplicated on different days. The reproducibility of the results was found always to be within 4% relative error and we report only average values. The reactor design and performance are discussed in the subsequent sections. For a typical experiment, the pilot plant was started-up by pumping distilled water to achieve the desired processing conditions including flow rate, pressure and temperature. Once the system reached steady state, the reactor feed was switched to the premixed algal slurry. The slurry tank was agitated to ensure homogeneity during the course of the experiments – samples from various locations within the tank showed variations <10% in the local biomass concentration.

In order to ensure steady-state operation and sampling, a minimum of 20 minutes of continuous operation was required for each data point. At each operating condition, two separate product samples (oil-water-solid mixtures) were collected in 500 ml Duran flasks downstream of the cooling and pressure let-down systems. Argon was injected into the gaseous product stream at a known rate to act as a tracer. The gas stream was analysed in triplicate (relative variation <5%) by micro gas chromatography (Varian 4900), allowing the gas species production rates to be determined and related to the input biomass flow on the basis of the measured argon concentration. It should be noted here that the pilot-plant was operated in some cases for up to 120 minutes and the product samples collected between 20-120 minutes were found to be consistent.

Since the biomass-to-water ratio in some runs was low, quantitative separation of the bio-crude floating on the water was sometimes difficult. Therefore, a standardised extraction with dichloromethane (DCM) was used in order to quantify the bio-crude yields gravimetrically. The oil-water-solids sample mixture (500 ml) was extracted for 60 minutes in a shaker flask with 100-350 ml DCM, after which the mixture was separated and filtered to isolate the bio-crude (dissolved in DCM), solids and aqueous phase fractions. The DCM solvent was allowed to evaporate over a 2-7 day period in a fume hood at room temperature. We confirmed that an additional period of 2-4 days produced no further weight change (within 0.01 g). Furthermore, we confirmed that solvent evaporation in a rotary evaporator gave the same results for oil yield. The yields were then calculated based on the recovered weight and are reported as a fraction of the dry ash-free feedstock. More details on separation and quantification can be found elsewhere [8].

The bio-crude fraction was analysed for elemental composition and boiling point distribution using simulated distillation thermal gravimetric analysis (sim-dis TGA, DTA-673, Stanton Redcroft, UK); 5-10 mg of sample was heated in 50ml/min of nitrogen to 900 °C at 10 °C/min. The HHV of the bio-crude was calculated from their ultimate analysis using the unified correlation proposed by Channiwala and Parikh [15]. Total organic and inorganic carbon (TOC, TIC) in the aqueous phase was determined using a TOC analyser (HACH- IL 550 TOC, Hach-Lange, Germany) by a differential method in which the TOC is calculated by subtracting the TIC from the total carbon. The analyses were carried out in duplicate, for which the maximum relative deviation was <2%, and we report the average result. Using the elemental composition of the bio-crude and solid residue along with the carbon content of the aqueous and gas phases, a carbon distribution was calculated.

The solid residue obtained after hydrothermal processing was air dried and then solvent washed with acetone to remove any residual bio-crude. Subsequently the solids were freeze dried (Christ Alpha 1-2

LDPlus, Christ, Germany) for 8 hours. The solid residue was then coated with a thin gold layer before analysis by scanning electron microscopy (SEM), (Zeiss EVO MA 15, Carl Zeiss Microscopy, Germany).

2.1 Pilot Plant Operation

The continuous flow hydrothermal biomass plant was designed and built in-house at the University of Sydney. The upper design temperature and pressure of the system are 350 ºC and 250 bar respectively which fall in the sub-critical region of water.

The process flow diagram of the plant is presented in Figure 1. Biomass slurry is pumped in two stages from stirred atmospheric-pressure batch tanks (Pumps 1 and 2 in Figure 1). Pump 1 is a low pressure screw pump (Range MD, Seepex, Germany) which provides the necessary suction pressure (2-6 bar) for the high pressure stage. Pump 2 is a GEA Niro Soavi model Ariete NS3006P triplex piston pump capable of delivering high viscosity fluids and slurries at pressures up to 600 bar and flow rates in the range 15 – 90 L/hr. The pumping rate is adjusted through the use of a variable speed drive; a mass flow meter (F in Figure 1) is used to measure the actual slurry feed rate.

The pressurised slurry (up to 250 bar) is partially preheated in feed-effluent exchangers HX1 and HX2 which capture some of the sensible heat of the product stream leaving the reactor. The heat exchangers HX1 and HX2 are coil-in-shell devices (FLF series sample cooler, Sentry Equipment Corp, USA) in which only the coils are rated for the maximum design pressure of the plant – for this reason, the hot products leaving the reactor are let down to ~10 bar downstream pressure control valve PCV (Type 1711 needle valve, Badger Meter Inc, Germany) before passing to the heat recovery section. In order to maintain the process water in the liquid state during this pressure let-down, the products are first cooled to ~170 °C via contact with a clean circulating water stream in heat exchanger HX3, the temperature of this circulating stream in turn being maintained by contact with cooling tower water in HX4. Back-pressure

regulating valve BPRV (KPB series, Swagelok Company, USA) is utilised to keep this line above the saturation pressure. After BPRV, the products are nominally at atmospheric pressure and are separated into gaseous and liquid streams for sampling and analysis. Gases and vapours are vented to atmosphere via activated carbon filters (ACF).

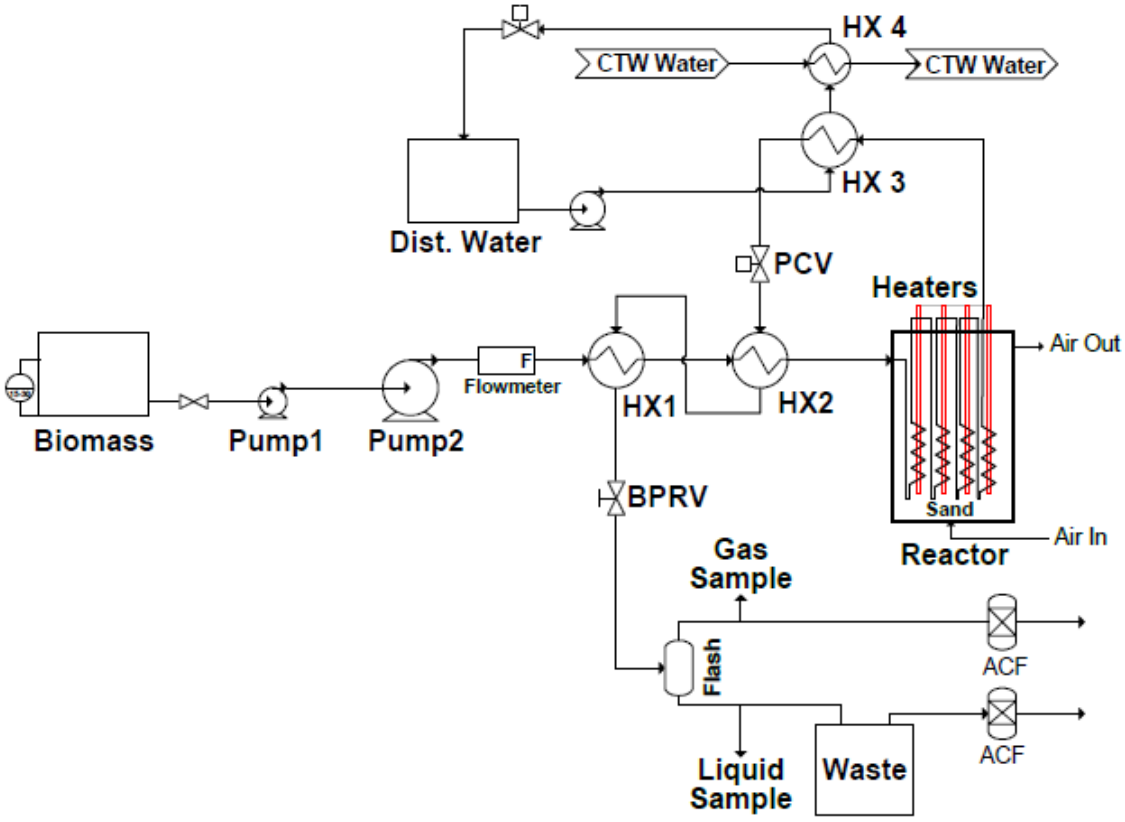

Figure 1: Process Flow Diagram (PFD) of hydrothermal biomass processing plant.

In order to alter the residence times of our experiments, the pump speed was changed and the overall residence times through the reactor coils were calculated based on the flow rate, density, pipe diameter and length.

The reactor is shown schematically in Figure 2. The reactor comprises of four stainless steel (grade 316) coils immersed into a heated fluidized bed. Depending on the reactor coil configuration, the plant can

provide residence times between <1 and 30 minutes; for this study, the coils (each 16 m in length, outer diameter 9.5 mm and wall thickness of 1.65 mm, total reaction volume ~2 L) are connected in series to enable reaction times between 2 and 8 minutes to be studied. Approximately 200 kg of alumina is fluidized by compressed air within the vessel. Heating is provided by 4×6 kW electric heating elements inserted into the fluidized bed.

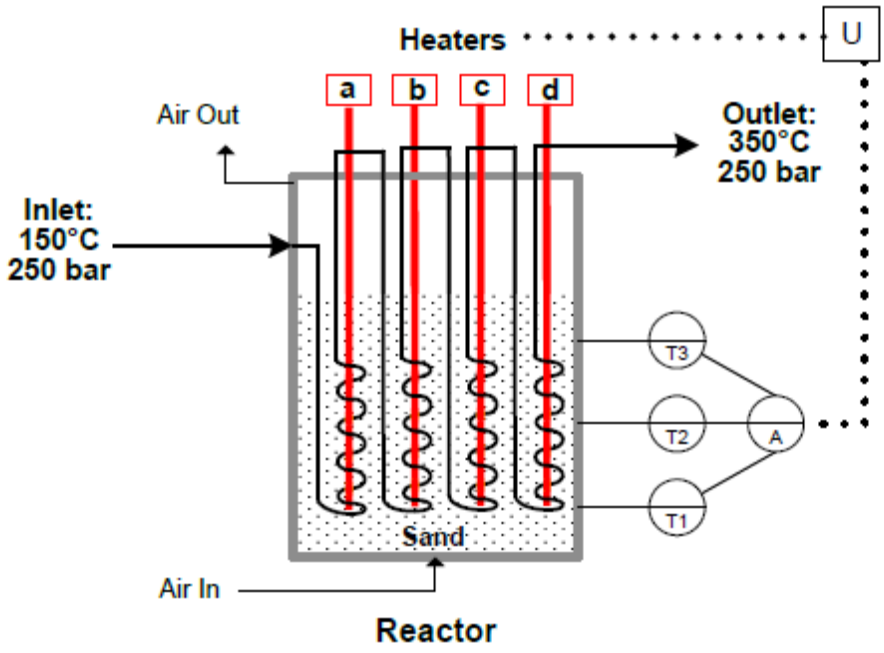

Figure 2: Schematic representation of flow-reactor configuration and control.

The entire plant is controlled via a distributed supervisory control and data acquisition (SCADA) system supplied by Yokogawa Australia Pty Ltd. Process variables including temperature, pressure and flow rate are specified by the operators through Yokogawa's FAST/TOOLS SCADA software. As illustrated in Figure 2, the average bed temperature is used to control the power input from the heaters into the system.

Pressure relief valves are utilised in the process as a safety measure in the case of a pressure build-up due to blocking or poor control resulting in a pressure overshoot. The control system has also been programmed to ensure that set pressures always exceed the saturation pressure of water at the temperature at which the system is operating at each point in time.

3 Results and Discussion

3.1 Reactor Performance

The performance of the continuous flow HTL reactor with respect to pressure, temperature and flow rate was examined. Pressure control in slurry systems exhibits an "inverse scaling" effect in that the smaller the system, the more difficult it is to maintain stable flows. Smaller flow rates such as in the present pilot plant demand smaller pumps which in turn have reduced valve seal tolerances; control valves similarly have smaller orifices – in both cases, there is an increased potential for flow disruption and blockage if particles are caught in the valves. This effect can make it difficult to pilot slurry processes – at the same time, conditions that give rise to particular behaviour, such as the formation of agglomerates or deposits, can be identified and allowed for when the process is implemented at larger scale.

Figure 3 (a) shows typical pressure-time traces obtained when processing 1 wt% Spirulina slurry at different temperatures, using a control valve (PCV in Figure 1) orifice size ~20 µm when fully open. Relative to pressure control with pure water feed, there are significant pressure excursions arising from transient blockage of the control valve. The pressure excursions are less severe at 300 ºC than at the lower temperatures studied. As shown in Figure 3 (b), increasing the residence time from 3 to 5 minutes at 300 ºC for 1wt% Spirulina was accompanied by a further significant improvement in pressure controllability, approaching the behaviour obtained with water alone. Both algae performed the same in this regard.

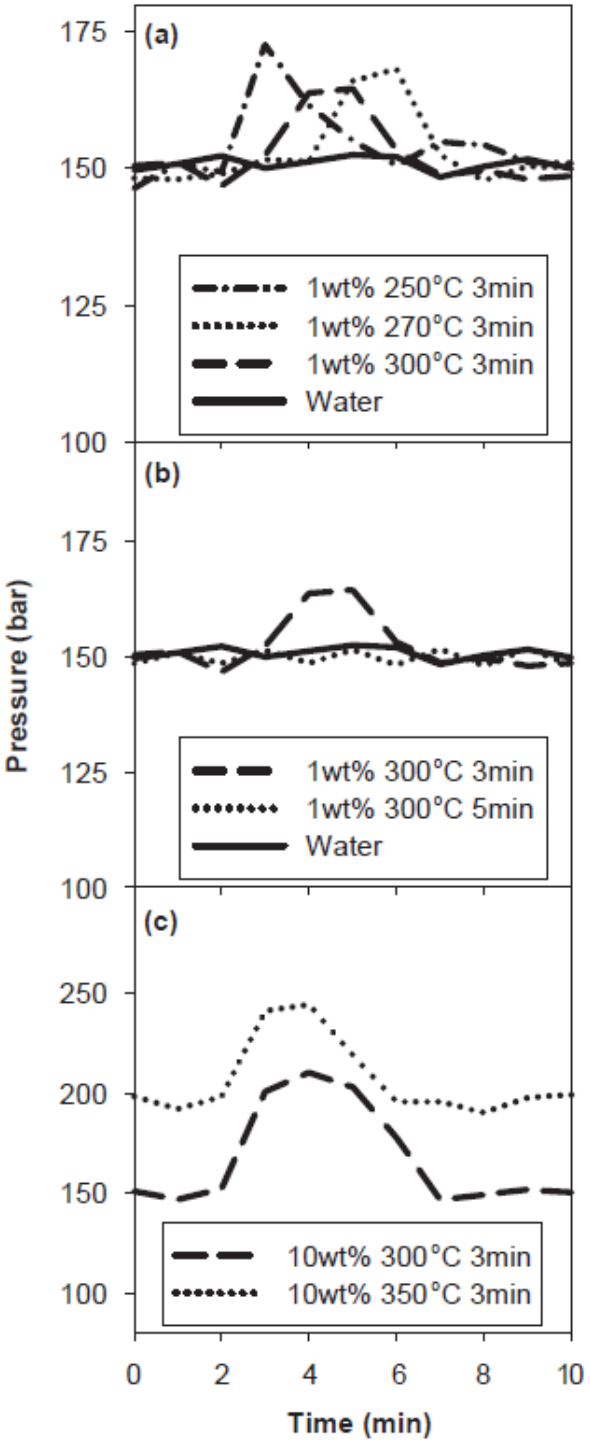

Figure 3: Pressure control for (a) 1 wt% Spirulina at 150 bar with varying experimental temperatures for a residence time of 3 minutes (b) 1 wt% Spirulina at 150 bar with varying residence times at 300 °C (c)

10 wt% Chlorella at 150 and 200 bar with varying experimental temperatures for a residence time of 3 minutes.

In order to process higher biomass loadings (>2 wt%), a larger control valve orifice (~90 µm when fully open) was required to avoid complete blockage that could not be cleared without shutting down the plant and disassembling the valve. Pressure traces for processing of 10 wt% Chlorella (Figure 3 (c)) show that significant, but self-clearing blockages occur even with the larger valve orifice. Here we note for completeness that blockage of the reactor coils themselves has never occurred in any of our operations, up to a maximum duration of 120 minutes in a single run.

It is believed that the more severe process conditions result in a more extensive conversion of the algal solids. This was observed for both strains, i.e. the solid yields from HTL consistently decreased with increasing temperature and residence time, as discussed in detail in section 3.3. It can be seen from Figure 3 (a-c) that the higher experimental temperatures correspond to smaller pressure fluctuations. Additionally, increasing the residence time from 3 to 5 minutes at 300 ºC for 1wt% Spirulina further decreased the solids yield and resulted in an improvement in pressure control. In fact, as depicted in Figure 3 (b) the pressure controllability was similar to that of clean water which is attributed to the more extensive conversion of algae solids to bio-crude and/or breakdown to water soluble material at the higher temperatures and residence times examined. At the greater biomass loading of 10 wt%, the solids loading is such that large pressure spikes are evident even when the reaction temperature is increased to 350 ºC. We were unable to process higher concentrations of these microalgae in our plant. Recognising the inverse scaling effect referred to previously, we can expect controllability to be improved in a larger-scale plant.

It should be pointed out that because the pressures in our system are always substantially greater than saturation, these pressure fluctuations are not accompanied by temperature fluctuations and are unlikely to have any significant impact on the course of the HTL reactions. The effect of pressure, beyond the

saturation value, on hydrothermal liquefaction of microalgae has previously been shown to have no effect on product yields in batch reactors [16].

The reactor temperature and biomass slurry feeding rate were also recorded during each run. The average temperature of the fluidised bed heater was at all times within ±3 ºC from the set point (250, 275 and 300 °C). The biomass slurry is expected to reach within 10 ºC of the desired temperature inside the first of the four helical reactor coils immersed in the bed heater. The overall residence time inside the reactor coils was determined by measuring the biomass slurry feeding rate and correcting for the change in density of the solvent in going from room temperature to the nominal reaction conditions. The slurry feeding rate was maintained to within ±4 % of the setpoint flow rates investigated in this study (15-30 L/hr).

3.2 Microalgae Feedstock Analysis

The feedstocks investigated were two commercially available microalgae, Chlorella and Spirulina. The analysis of the feedstock is presented in Table 1; the biochemical composition was provided by the supplier, all other data were obtained in the laboratory. Both strains had similar ash (<8%) and moisture (<6%) contents, those of Spirulina being marginally higher in each case. The HHV of the algal biomass was in the range of 24-25 MJ/Kg; the slightly lower HHV for Chlorella results from the fact that Chlorella contains greater amounts of oxygen and lower levels of carbon and hydrogen. The lipid contents of both strains are low (<10%) as the microalgae were grown as food supplements rich in protein rather than as sources for biofuels (for which a higher lipid content is especially beneficial for biodiesel production). As presented in Table 1, the protein content of the microalgae was in the range of 60-68%, Spirulina contained a larger fraction of protein leading to the higher nitrogen content of 12.1 wt%.

Table 1: Analysis of microalgae feedstock.

	Chlorella	**Spirulina**	**Metals (ppm w/w) (daf)**	**Chlorella**	**Spirulina**
Proximate analysis (wt% as received)			Al	25	402
Ash	6.0	7.6	Ca	1922	7782
Moisture	5.2	5.7	Cl	3946	4433
Elemental composition (wt% daf)			Cu	6	8
C	53.5	53.7	Fe	846	879
H	7.4	7.7	K	11705	13899
N	11.0	12.1	Mg	3288	4256
S	0.5	0.6	Mn	57	56
O*	27.6	25.9	Na	860	4732
Biochemical content (wt%)			Ni	0.7	2.6
Carbohydrates	25	11	Zn	21	27
Protein	60	68			
Lipids	4	8			
HHV (MJ/Kg)	24.3	24.9			

daf= Dry Ash Free; *=By difference; Proximate and elemental analyses tested in duplicates for each sample and the maximum deviation = ±0.3.

Metal analysis by ICP shows the main constituents of the ash fraction to be K, Mg and Ca. The presence of potassium has been reported to be significant as it can be used as a catalyst in hydrothermal media. For

example, potassium carbonate can result in reduced solid residue when processing wood in HTL, while potassium hydroxide can promote water-gas shift reactions during hydrothermal gasification [17, 18]. K, Fe and Mg are also minor nutrients required for microalgae growth, hence in order to recycle the process water post HTL for algae cultivation, it is desirable that these nutrients report to the water phase. Nickel on the other hand, also present in the algal biomass and possibly deriving via leaching from reactor walls during HTL [19], acts as a growth inhibitor and therefore needs to be monitored.

The chloride content was also measured. Chloride poses a risk to pressure vessels constructed from austenitic stainless steels under HTL conditions because of the possible occurrence of chloride stress corrosion cracking, even at ppm levels of the ion. It is monitored routinely at the pilot plant facility as part of our materials evaluation – it is expected that the choice of reactor material will be especially important when processing marine algal strains because of the high chloride loading that will arise.

The microalgae were in addition analysed for their particle size distributions as these have an influence on the reactor performance. In particular, as discussed above, the needle control valve and the back pressure regulator can become blocked if the particle size flowing through them is too large. This can be avoided if the reaction conditions are severe enough to break down the algal cell structure to smaller fragments.

Figure 4 shows the size distributions of the two strains. Chlorella has a narrower distribution and a smaller average particulate size. The volume median diameter of Chlorella and Spirulina are 48.4 and 62.2 μm respectively. Since the larger Spirulina algae were associated with less difficulty in controlling the reactor pressure (discussed above in section 3.1), it is apparent that the initial particle size of the algae feed is less important than the behaviour of the cells and how easily they can be broken down to smaller fragments in the reactor. The viscosities of the algae slurries at 40 ºC for 1 and 10 wt% solids concentrations were found to be ~0.9 and ~2.9 mPa.s respectively – in both cases the presence of the

algae leads to a significant increase in viscosity relative to that of water at the same temperature (0.65 mPa.s).

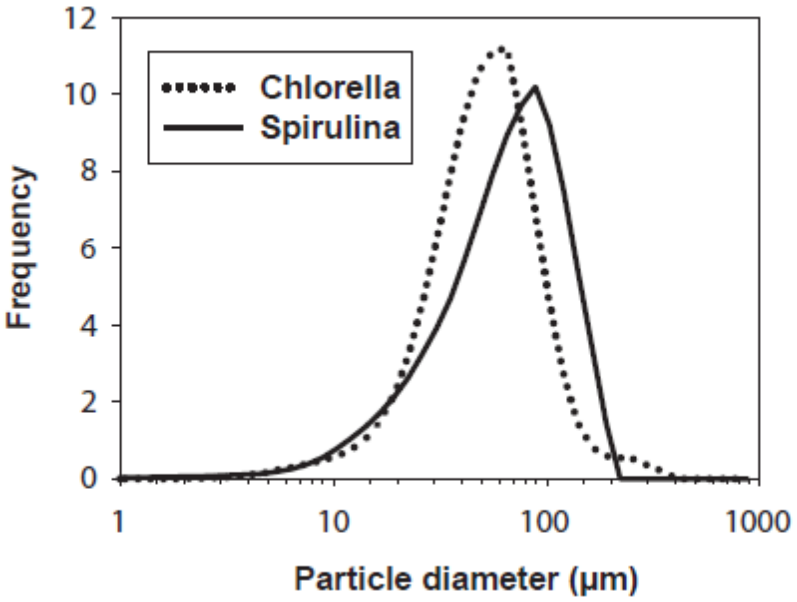

Figure 4: Size distribution of dehydrated microalgae prior to hydration and hydrothermal processing.

3.3 Hydrothermal Liquefaction Results

The results obtained from processing Chlorella and Spirulina in the continuous HTL reactor are presented in Figure 5 (a-b) on a dry ash free (daf) basis. Overall, higher temperatures and longer residence times increased the yields, in agreement with results of batch HTL experiments on microalgae [11].

Feed concentrations in batch HTL studies [11, 20] have been shown to have minimal effect on the product yields, but it is clear from Figure 5 that yields at the lowest concentrations employed in this work (1 wt% biomass) are significantly lower than those at higher concentrations. Only above about 5 wt% do the yields become essentially independent of slurry concentration – the losses arising at lower concentrations are considered in more detail in terms of the overall carbon balance in section 3.3.3.

Under mild processing range (250 °C for 3 minutes), the bio-crude yield from the two strains was below 10 wt%, presumably corresponding to extraction only of the lipids present in the algae. Under more severe processing conditions, yields increase significantly as the hydrothermal liquefaction of proteins and carbohydrates begins to contribute to the bio-crude. The maximum yield obtained was 41.7 wt% from Chlorella with a feed concentration of 10 wt%, processed at 350 °C for 3 minutes residence time. Garcia Alba et al. [21] achieved similar bio-crude yields from microalgae Desmodesmus sp. in a batch reactor – for example, with a 5 minutes residence time at 350 °C and ~9.5 wt% solids loading, the bio-crude yield was found to be 45.3%; Jena et al. [11] found 33% at this temperature when processing Spirulina platensis in a batch reactor for 60 minutes at 10 wt% solids loading.

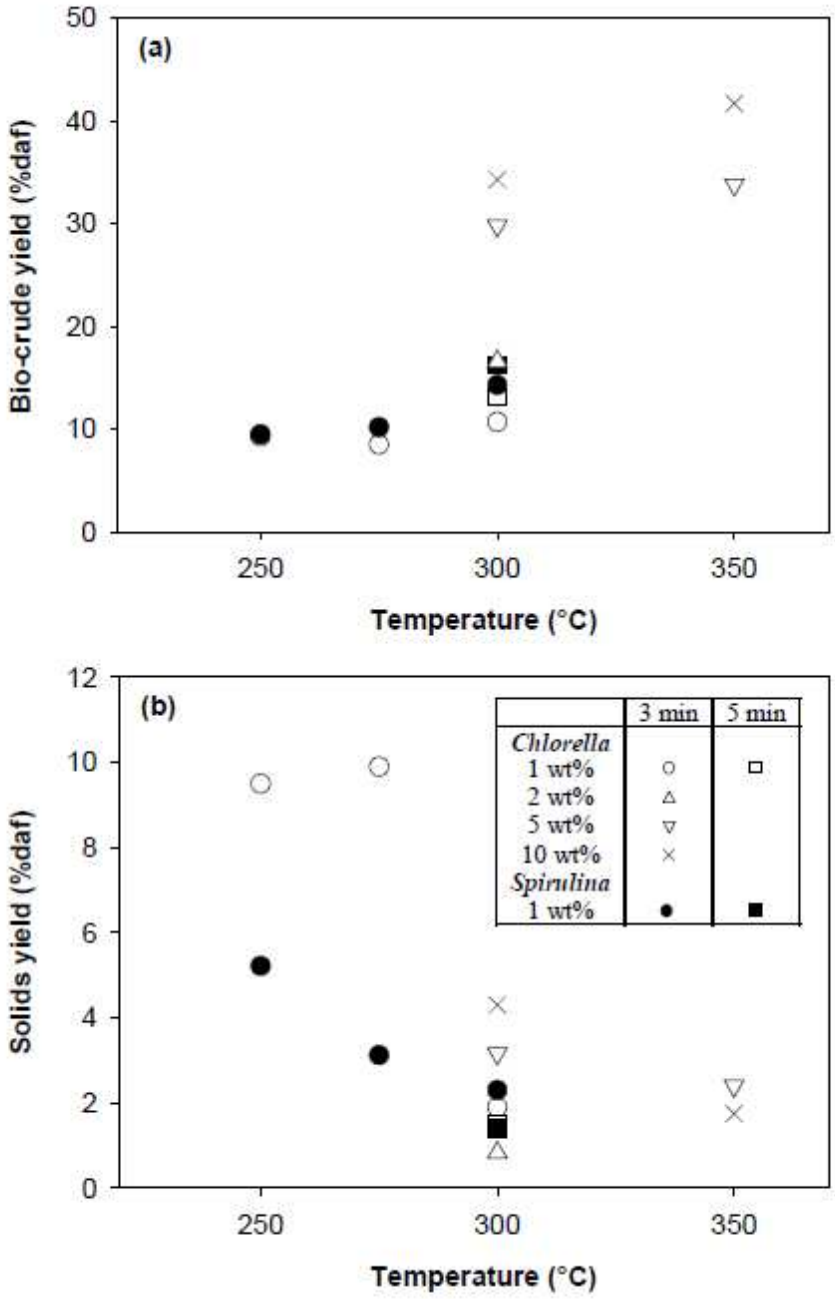

Figure 5: Yields of products for the different hydrothermal liquefaction experiments (a) bio-crude (b) solids residue. Results are an average of at least two duplicates; maximum relative error is 4%.

daf= Dry Ash Free.

The effect of increasing residence time at the lower biomass loadings had minor impact on the bio-crude yields obtained from both strains and thus was not further investigated at the higher concentrations. Under slowly-heated batch HTL conditions, the residence time for maximal bio-crude production has been reported to be in the range 15 minutes (brown macroalgae, [20]) to 60 minutes (Spirulina platensis, [11]). Although these optimal times appear to be significantly longer than we find, the batch studies show peaks in the yield to be relatively weak; we also note that the long heating times associated with batch studies means that results from these diverse studies should be compared only cautiously. In particular, we note that rapidly-heated batch HTL shows greater bio-crude yields at 5 minutes than at 60 minutes [21]. What is clear in our results is that the solids fraction of the products is already very low under our most severe conditions (350 °C for 3 minutes residence time) and that the potential for increasing yield at longer residence times is very limited. We therefore conclude that the present results suggest that the maximal yield of bio-crude may be obtained in much shorter residence times under continuous flow conditions than batch studies have suggested. However, we also note that the composition of the bio-crudes may differ between short and long processing times, depending on the extent, for example, to which the oxygen content of the bio-crude is reduced by the HTL process. The maximal yield may not be optimal in terms of properties of the bio-crude.

3.3.1 SEM Analysis

Scanning electron microscopy (SEM) was utilised in order to investigate the visual appearance of the algae cells and the solids residue component after liquefaction in the continuous flow reactor. It is expected that the reactor performance and the bio-crude yields obtained are linked to the algae cell structure being increasingly disrupted with more severe processing conditions. Bio-crude yields were increased with higher temperatures and at the same time the solids residue component was decreased. Additionally, as discussed in section 3.1, the reactor performance with respect to pressure fluctuations was improved with higher processing temperatures.

The SEM images of Chlorella pre- and post-liquefaction are presented in Figure 6 (a-d). Fresh Chlorella cells with a 3000x magnification prior to processing are shown in Figure 6 (a). The cell clusters have a diameter of around 55 µm which fits well with the data obtained by particle size distribution. Figure 6 (b) shows the solids residue obtained at 250 ˚C: it can be seen that the selected residue particle is much larger (>500 µm) than an individual cell, indicating that cells have agglomerated to form a solid compact structure with filamentous strings. The cell walls seem to have broken at these conditions as there is no apparent resemblance to the original cell. The pronounced agglomeration to a compact structure suggests that reactor performance will be influenced by the large particles present under these conditions.

Increasing the temperature to 275 ˚C with the same residence time sees the disappearance of the filaments observed at the lower temperature. The overall structure of agglomerated cells remains intact but appears less compact with a less uniform surface morphology. The diameter of the agglomerate is approximately 300 µm, similar to the particle size observed at 250 ˚C. In the final image, the solid residue obtained from processing Chlorella at 300 ˚C and a residence time of 3 minutes is presented. The cell structure appears to be completely destroyed; the larger structure seen in Figure 6 (d) is approximately 10-15 µm, fragments of smaller sizes (<10 µm) can be seen in the background. We conclude that at 300 ˚C the

breakdown of the original cells is largely completed, leading to an improved bio-crude yield and a reduced solids residue, which in turn reduces the magnitude of pressure fluctuations.

Garcia Alba et al. [21] performed similar analysis on the cells of Desmodesmus sp. after HTL for 5 minutes in batch experiments. The SEM images presented show the solid residue component post-HTL in the temperature range of 175 to 275 ˚C. It appears that the Desmodesmus sp. cells perform similarly to those of Chlorella as they seem to agglomerate to clusters after liquefaction. However, they exhibit filaments in their fresh form which appears to hold the cell clusters together at different processing conditions. In the current study, filaments are not present in the fresh algae and, hence, their origin is unknown. Garcia Alba et al. concluded from their SEM analysis that cell breakage occurred at 250 ˚C when processed for 5 minutes. Cell breakage also appears to have occurred at the same temperature and comparable residence time in the current study, with agglomeration observed at less severe conditions.

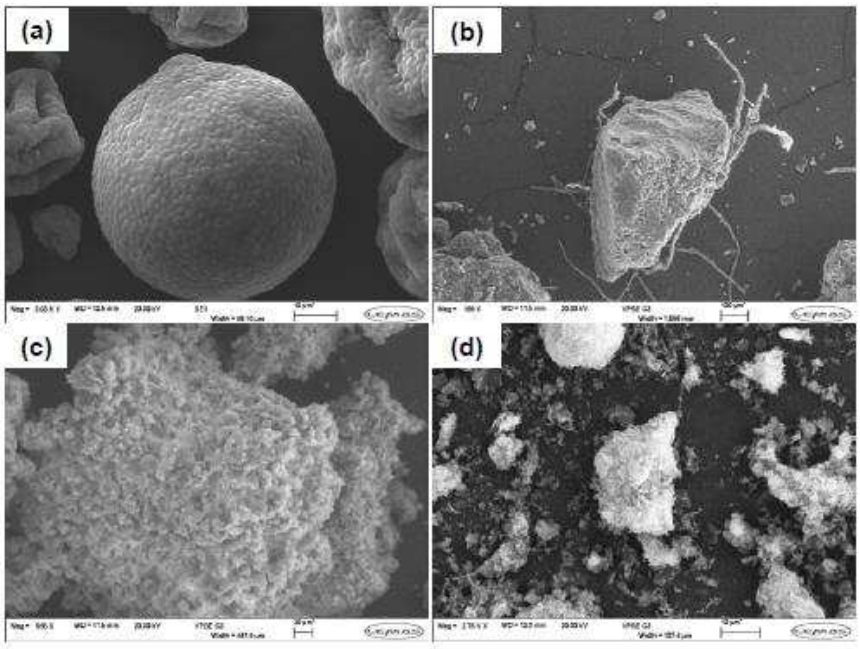

Figure 6: SEM images of Chlorella (a) dry unprocessed (b) processed at 250˚C 3 min (c) processed at 275˚C 3 min (d) processed at 300˚C 3 min. 1wt% solids concentration and 150 bar system pressure.

3.3.2 Bio-crude Analyses

The recovered bio-crude was analysed for its elemental composition and the data are presented in Table 2. The oxygen contents ranged from ~21 to 12 wt%, significantly lower than the initial values in the raw feedstock (~30 wt%). Overall, more severe processing conditions led to a greater reduction in the oxygen content. The biomass loading on the other hand had no effect on the bio-crude quality, in agreement with results published by Jena et al. [11] on a batch reactor system.

Table 2: Elemental analysis (wt% daf) and Higher Heating Value (HHV) of bio-crudes from hydrothermal liquefaction of Chlorella and Spirulina at different processing conditions.

Chlorella	**Temp.**	**Res. Time**	**C**	**H**	**N**	**S**	**O***	**HHV (MJ/kg)**
1 wt%	250°C	3.0	70.3	4.8	2.6	0.4	21.9	27.9
	275°C	3.0	65.9	9	4.3	0.8	20	31.6
	300°C	3.0	64.1	7.8	7.5	1.5	19.1	29.6
	300°C	5.0	67.6	8.2	6.3	2.1	15.8	31.7
5 wt%	300°C	3.0	69.5	8.9	7.2	(a)	14.4	33.2
	350°C	3.0	67.9	8.9	7.9	(a)	15.3	32.5
10 wt%	300°C	3.0	69.1	8.7	7.8	0.9	13.5	33.0
	350°C	3.0	70.7	8.8	7.7	0.8	12.0	33.8
Spirulina								
1 wt%	250°C	3.0	65.8	8.5	3.5	0.5	21.7	30.7
	275°C	3.0	62.3	7.3	6.7	1.1	22.5	28.0
	300°C	3.0	64.3	8.4	7.5	1.3	18.5	30.4
	300°C	5.0	68.3	8.3	6.9	1.1	15.4	32.0

*= By difference; (a)= Not analyzed; Elemental analysis tested in duplicates for each sample and the maximum deviation = ±0.3.

The elemental analyses of the bio-crudes also showed an increase in the nitrogen content at higher processing temperatures used, indicating an increase in the production of bio-crude from the protein fraction of the algae. These trends are consistent for both strains of microalgae. For a residence time of 3 minutes, processing of Chlorella at 250 °C yielded bio-crude with a nitrogen content of 2.6 wt%, whereas at 300 °C this value was 7.5 wt%. These high nitrogen contents constitute a problem for the derived bio-

crudes because they limit their direct usability as a fuel (because of NOx emissions) and may poison catalysts in conventional refining processes. Upgrading is therefore essential in order to reduce the nitrogen content. Catalytic upgrading could in principle be used in order to remove the nitrogen through hydrodenitrogenation, however this is a costly process which has not been demonstrated on feedstocks such as these. It has been suggested that to produce a bio-crude with lower levels of nitrogen, the use of heterogeneous catalysts needs to be considered during liquefaction [22, 23]. Another route proposed is to extract the protein fraction of the algae prior to subjecting it to the high temperature HTL process in a biorefinery concept [21].

The HHVs of the bio-crudes ranged from 27 to 34 MJ/kg. This represents a significant increase from the HHV of the algal biomass feedstock (~24 MJ/kg). The Channiwala and Parikh correlation [15] used in this study has been validated for fuels with a wide range of elemental compositions, specifically it has been established for materials with oxygen levels of up to 50% and nitrogen levels of 5.6%. The Du-Long formula, which is more frequently found in literature does not include nitrogen and is only accurate for low oxygen levels. On average the Channiwala and Parikh correlation gave HHVs 0.3% lower than those calculated using the Du-Long formula for bio-crudes obtained in this study. The observed increase in the HHVs from the biomass to the bio-crude is due to the reduction in oxygen and higher relative carbon contents. The aim should be to reduce the amount of oxygen to increase the HHV, while simultaneously decreasing the levels of nitrogen in order to reduce emissions or refinery processing costs. Petroleum crude oil contains <1 wt% oxygen and nitrogen and has HHV > 40 MJ/kg which implies that bio-crude produced from microalgae through both batch and continuous flow HTL processes requires upgrading prior to further processing.

To determine the boiling point distribution of the bio-crudes a simulated distillation was carried out by TGA and is presented in Figure 7 for Chlorella (a) and Spirulina (b). The majority of the bio-crude falls in the distillation range of Vacuum Gas Oil (VGO). Higher processing temperatures and longer residence

times resulted in larger amounts of low boiling point material. The greatest yield of the low boiling fraction, corresponding to Heavy Naphtha, is obtained at 300 °C and 3 minutes residence time. Generally, the distribution is much more uniform than obtained by Vardon et al. [9] who found the majority of bio-crude to fall in the VGO region (~50%) for Spirulina processed in a batch reactor at 300 °C for 30 minutes. They also found the material reporting to the Heavy Naphtha fraction to be below 5% and that to the Kerosene and Gas Oil fraction between 10-15%.

The bio-crudes obtained from Chlorella in the continuous flow HTL reactor were additionally compared to those obtained from processing Chlorella at 350 °C for 60 minutes in a batch reactor from a previous study by Biller et al. [23]. Figure 7 (a) shows that the trends observed for the continuous flow system also apply for the higher temperature and longer residence time obtained in the batch process; the residue fraction is further decreased and the lighter fractions increased. The very heavy boiling point material is reduced with increased severity of the processing conditions. The sim-dis data illustrate that the more severe processing conditions are favourable as they lead to an increased yield of lower molecular weight bio-crude fraction.

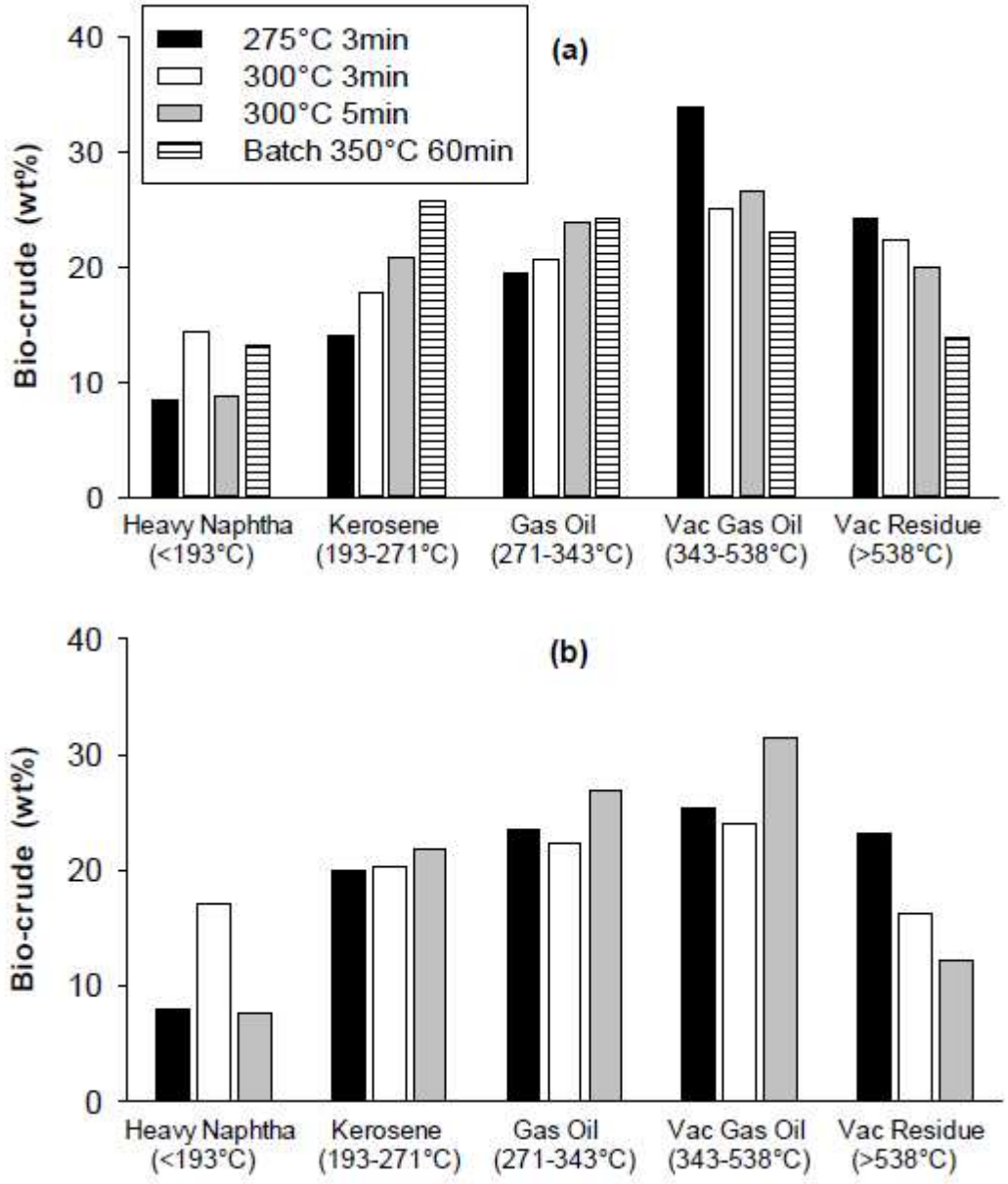

Figure 7: Simulated distillation by TGA for bio-crudes derived from (a) Chlorella and (b) Spirulina.

3.3.3 Carbon Balance in Product Streams

Figure 8 shows the distribution of carbon in the different product phases calculated using the yields and elemental compositions of the bio-crude, solids residue and gaseous product streams along with the carbon content of the aqueous phase (by TOC analysis). In most runs, the gas phase was analysed by gas

chromatography as described in section 2; for the remaining few cases, the gas yield is lumped with the undetermined "loss" which also incorporates net errors.

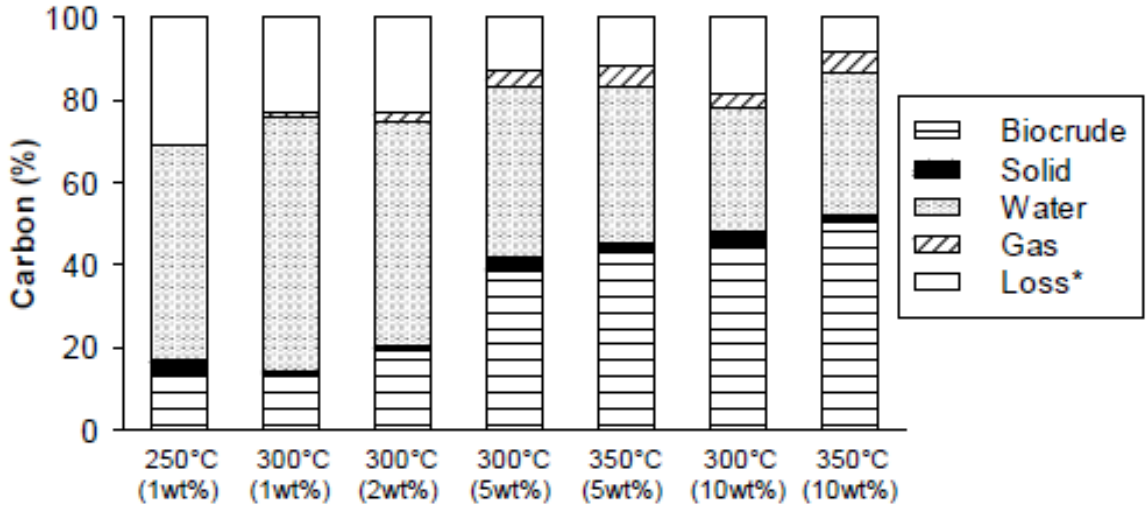

Figure 8: Carbon balance from the continuous HTL of Chlorella at various feed concentrations and temperatures for 3min residence time. Gas was not analysed for processing 1 wt% at 250 °C.

*= By difference.

It is clear that a substantial fraction, up to 60%, of the carbon reports to the aqueous phase, principally (>90%) as organics (data not presented). Processing Chlorella and Spirulina with a 1 wt% feed concentration at the various HTL conditions resulted in similar trends for both strains with the largest carbon fraction reporting to the process water. It appears however that with the higher biomass loadings, as depicted in Figure 9, the carbon recovery to the aqueous phase decreases significantly, from 61% at a feed concentration of 1 wt% and 300 °C to 30% at 10 wt% feed concentration. Jena et al. [11] come to a similar conclusion in their study of the microalgae Spirulina platensis with feed concentrations between 10-50 wt% in a batch reactor at 350 °C for 60 minutes. Although the range of their solids loading is considerably higher than that investigated in this study, a decrease in the water solubles yield, from ~45 to 30%, is evident in going from 10 to 50 wt% feed concentration. These results could arise perhaps through

equilibrium limitations (such as limited solubility in the water phase) that become more apparent at higher feed concentrations. More detailed chemical analysis of these dissolved organics is needed to understand the observations and will be the focus of future research.

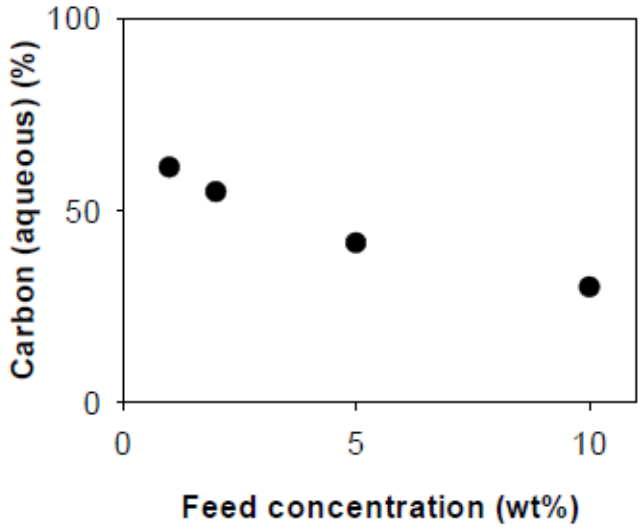

Figure 9: Carbon recovery to the aqueous phase for Chlorella processed at 300° C, 3 minutes residence time and varying feed concentrations.

The large carbon fraction in the water clearly impacts the economic feasibility of the HTL process. Ross et al. [14] have suggested using the organic carbon in the aqueous phase as a substrate for mixotrophic growth for microalgae cultivation. The aqueous phase from the current study was also analysed for metal content by ICP and showed that there were high levels of K, Na, Ca and other minor nutrients (results not presented). Additionally, results from literature have previously shown that the water is high in nitrogen and phosphorous which are nutrients required for algae growth [14, 24]. Alternatively, Frank et al. [25] suggest in their recent life cycle assessment of HTL of microalgae that the aqueous organic carbon could be used to produce H_2 via catalytic hydrothermal gasification. This H_2 can then be used for upgrading the bio-crude.

The gas stream separated from the products was predominantly CO_2, consistent with its generation principally via decarboxylation reactions. For 10% biomass loading, the proportion of CO_2 decreased from 99 mol% to 95 mol% as the temperature was raised from 300 °C to 350 °C; across the whole range, the only other gas present in measurable concentrations was CO. Figure 10 shows that the carbon recovery to the gas phase increased with higher temperatures and feed concentrations to a maximum of 5% for Chlorella at 350 °C, 3 minutes residence time and a 10 wt% feed concentration. These results may be compared with those of Garcia et al. [21] who reported a gas yield of 15.1 wt% with a CO_2 concentration up to 99.7 mol% for batch processing of Desmodesmus sp. (9.5 wt%) at 350 °C for 5 minutes reaction time. These results correspond to a carbon recovery of ~8% to the gas phase which is somewhat greater than we find, possibly because the reaction time is not only greater than ours but is based on the time at temperature, ignoring significant heating and cooling times during which additional reaction will very likely have been occurring.

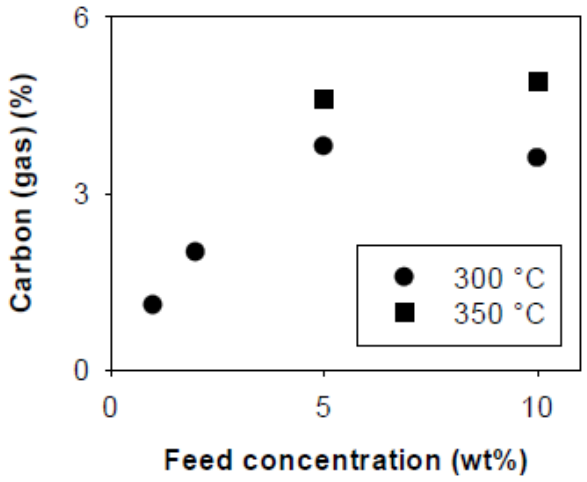

Figure 10: Carbon recovery to the gas phase for Chlorella processed at 300-350 °C, 3 minutes residence time and varying feed concentrations.

As shown in Figure 8, while the carbon recovery to the bio-crude increases significantly with biomass loading, especially in going from 2% to 5% loading, the unaccounted carbon (loss) correspondingly

decreases from 30% to <10% over the range of biomass loadings studied. It is apparent that some of the oil yield is being lost to the system at the lowest loadings. We have confirmed that there is some hold-up of oily solids in the shell-side of the heat exchangers HX1 and HX2 and we believe that this is sufficient to impact the oil yield measurements at the lowest loadings (<2%). It is not practical to recover the oil held up in the system but results at higher loadings are unlikely to be affected because of the greater flow of oil in these cases.

We believe that the oil that is recovered at low loadings remains representative of the actual product under these conditions. Changes in the carbon content of the crude across the range of our experiments are generally small, in part because temperatures that favour oxygen removal lead also to a greater accumulation of nitrogen. The effect of temperature on the carbon recovery in the oil is apparent at 10% loading, the recovery increasing from 44% to 50% in going from 300 to 350 °C. Previous batch HTL studies under both short (5 minutes for Desmodesmus sp., [21]) and long (60 minutes for Nannochloropsis sp., [10]) residence times between 250-350 °C show similar results in which the increase in the carbon recovery with rising temperature is attributed to increasing yields while the carbon content of the bio-crude is largely unchanged.

4 Conclusions

This work demonstrates the successful operation of a continuous flow pilot-scale HTL reactor system and provides insight into the processing of microalgae under sub-critical conditions. The bio-crude yields reached a maximum of 41.7 wt% for Chlorella processed with a 10 wt% solids concentration at 350 °C, 3 minutes residence time and 200 bar. Overall, more severe conditions increased yields, reduced the oxygen content and led to an increased formation of a lower molecular weight bio-crude fraction. It was also

shown that the higher processing temperatures increased nitrogen levels as more of the protein present in the algae was liquefied and converted to bio-crude.

The distribution of carbon in the product phases showed an increase in carbon recovery to the bio-crude with more severe processing conditions and higher biomass feed concentrations. A maximum of 50.5% carbon recovery for Chlorella with a 10 wt% feed concentration at 350 °C and 3 minutes was obtained. A considerable amount of organic carbon was also found in the process water. Conversely, the carbon fractionation to the solids residue component was small across the range of conditions investigated and was found to decrease with higher temperatures and longer residence times.

The performance of the continuous flow HTL reactor with respect to pressure, temperature and flow rate was also examined. Higher processing temperatures and longer residence times improved the pressure controllability. It was concluded that greater solid yields and larger particles caused difficulties for the control valve under less severe processing conditions. Flow rate and temperature control on the other hand were not affected with the varying operating conditions.

Overall, this work has confirmed that the general trends observed in batch experiments apply also to continuous processing. However, given the uncertainties around heating and cooling times in batch reactors, it is not surprising that the reaction timescales obtained from the batch experiments are often very different from those obtained under continuous flow conditions. Further development of continuous flow processing must also take into account the pumpability and behaviour of the biomass slurry, although these factors are difficult to trial in small-scale systems.

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