



Process development for hydrothermal liquefaction of algae feedstocks in a continuous-flow reactor

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ABSTRACT

Wet algae slurries can be converted into an upgradeable biocrude by hydrothermal liquefaction (HTL). High levels of carbon conversion to gravity separable biocrude product were accomplished at relatively low temperature (350 °C) in a continuous-flow, pressurized (sub-critical liquid water) environment (20 MPa). As opposed to earlier work in batch reactors reported by others, direct oil recovery was achieved without the use of a solvent and biomass trace components were removed by processing steps so that they did not cause process difficulties. High conversions were obtained even with high slurry concentrations of up to 35 wt.% of dry solids. Catalytic hydrotreating was effectively applied for hydrodeoxygenation, hydrodenitrogenation, and hydrodesulfurization of the biocrude to form liquid hydrocarbon fuel. Catalytic hydrothermal gasification was effectively applied for HTL byproduct water cleanup and fuel gas production from water soluble organics, allowing the water to be considered for recycle of nutrients to the algae growth ponds. As a result, high conversion of algae to liquid hydrocarbon and gas products was found with low levels of organic contamination in the byproduct water. All three process steps were accomplished in bench-scale, continuous-flow reactor systems such that design data for process scale-up was generated.

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1. Introduction

Hydrothermal liquefaction (HTL) of biomass provides a direct pathway for liquid biocrude production. This liquid product is a complex mixture of oxygenated hydrocarbons and, in the case of algae biomass, it contains substantial nitrogen as well. Hydrothermal processing utilizes water-based slurries at medium temperature (350 °C) and sufficient pressure (20 MPa) to maintain the water in the liquid phase. The processing option is particularly applicable to wet biomass feedstocks, such as algae, eliminating the need to expend energy to dry the feed before processing, as is required in other thermochemical conversion processes.

Elliott recently reviewed the early work in hydrothermal processing of wet biomass for both liquid and gas production [1]. Recent reports in the literature that have described HTL and its application to algae have been primarily related to batch reactor tests (see the long list in Chow et al. [2]). There have been reports of continuous-flow reactor tests for hydrothermal gasification of algae, both sub-critical liquid phase [3] and super-critical vapor phase [4]. Here we report the preliminary results of continuous-flow reactor studies of hydrothermal liquefaction with wet algae feedstocks. Subsequent

hydrotreatment of the HTL product oil demonstrated continuous-flow production of hydrocarbon fuel components while catalytic treatment of the aqueous phase in a separate continuous-flow reactor demonstrated fuel gas production from the dissolved organics. The generation of a relatively clean aqueous byproduct suggests the potential for recycle with dissolved nutrients to the algae growth medium.

1.1. Background

The use of hydrothermal processing (high-pressure, high-temperature liquid water) has received relatively limited study [1]. Although process development of hydrothermal liquefaction of biomass for fuel production can be traced to the work related to the Albany, Oregon, Biomass Liquefaction Experimental Facility, significant development has languished in the U.S. for the last three decades. HTL was recently included in the National Advanced Biofuels Consortium [5] program of work following a resurgent project at PNNL with ADM and Conoco-Phillips [6]. This article provides additional results of liquefaction using wet algae slurries.

Recently algae biomass has received a very high level of interest as a renewable biomass resource for fuel production because of the relatively high growth rates attained [7]. The primary focus has been the recovery of the fatty acid triglycerides produced by the

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algae as a feedstock for biodiesel production. However, not all algae are high fatty acid producers, and those that are, must be grown under controlled conditions, which are less than optimal growth conditions in order to maximize fatty acid production. An alternative algae utilization strategy is to grow algae in a wild and/or mixed culture at optimum growth conditions in order to maximize total biomass without consideration of fatty acid production. An appropriate biomass conversion process to utilize such algae without drying is desired to minimize parasitic energy requirements. Hydrothermal liquefaction can be used in this application for biocrude production from algae [8], utilizing both the lipid components but also the balance of the biomass structure as source material for oil production. The conversion of both biomass biopolymers (carbohydrates and protein) as well as lipid structures to a liquid oil product at hydrothermal conditions is expected [9].

Yokoyama's group at the National Institute for Resources and Environment in Japan (Dote et al. [10] and Minowa et al. [11]) published the first reports of hydrothermal liquefaction of microalgae (*Botryococcus braunii* and *Dunaliella tertiolecta*) using a batch reactor fed with high concentration dry matter algae mass, 50 wt.% and 78.4 wt.%, respectively. At 300 °C they reported oil yield of 37 wt.% and 57–64 wt.%, respectively for the two algae types. There has recently been a spike in reports on hydrothermal liquefaction of wet algae biomass. Ross et al. [12] at the University of Leeds in the UK, also a Chinese group [13] and a European group [14], groups at the University of Illinois [15] and Georgia [16], and Savage's group at the University of Michigan [17] have revisited HTL of algae. In their work similar processing conditions have been evaluated with different algae, *Chlorella vulgaris* and *C. pyrenoidosa*, *Nannochloropsis oculata*, *Scenedesmus dimorphus*, *Porphyridium cruentum*, *Desmodesmus sp.* as well as *Chlorogloeopsis fritschii* and *Spirulina* cyanobacteria. These reports develop a consensus that a wide range of microalgae can be processed by this route into a complex mixture oxygenated hydrocarbons that is liquid at or near room temperature at a high mass yield, including not only the lipid structures but the other biomass as well. Thus far the reports of all these groups have been limited to batch reactor testing. Although they have investigated the range of operating conditions in more detail than the earlier work, the results are still of limited value for developing an industrially useful continuous-flow process. In addition, the use in most cases of small batch reactors led the investigators to the use of solvents for the recovery of their oil products, thus complicating the determination of the oil yield and distorting its composition and properties by the inclusion of solvent-extractable, water-soluble components. A very recent report now available [18] describes continuous-flow operations of algae HTL. However, in those tests a low concentration of algae in water slurry, 1 to 10 wt.% of *Chlorella* or *Spirulina*, was evaluated and the operators chose to recover the biocrude by a solvent extraction.

The work at PNNL has focused on bench-scale testing in a continuous-flow reactor system in which the biocrude was recovered by gravity separation without the requirement of solvent handling. The work has been performed as part of the National Alliance for Advanced Biofuels & Bioproducts (NAABB), whose mission is to lay the technical foundations for a scalable, responsible and affordable renewable biofuel industry based on algae feedstocks [19]. The results reported here were performed as part of NAABB as an outgrowth of the original scope of work on hydrothermal gasification [20].

2. Methods and material

The equipment and procedures described below were used for testing the hydrothermal liquefaction of wet algae slurries as well as hydrotreating of the biocrude produced and the catalytic hydrothermal gasification of the organics left in the byproduct water stream.

2.1. Hydrothermal processing

A continuous-flow reactor system was originally designed for obtaining engineering data for the catalytic hydrothermal gasification (CHG) process and has been described in the literature previously [20]. The system essentially consists of the high-pressure pump feeding system, product recovery system, the 1-liter stirred tank preheater and the 1-liter tubular catalytic reactor. The mineral separation and sulfur stripping were done via two 1-liter high-pressure vessels in line between the preheater and the tubular reactor. The system was based on a throughput of 1.5 l of slurry per hour and was typically operated over a test period of 6–10 h. The process flow diagram is shown in Fig. 1. The modifications implemented for handling minerals and sulfur in the algae feedstocks are indicated in the outline labeled "NEW."

Essentially the same reactor system was used for HTL except with the omission of the catalyst bed in the tubular reactor and plumbing modifications to allow biocrude liquid product separation from the aqueous byproduct stream and the collection of both. The HTL configuration is shown in Fig. 2.

The algae feedstock preparation method was designed to ensure a relatively homogeneous feed for the reactor. The feedstocks were acquired as dewatered paste and the small cellular structure of the algae allowed simple mixing involving only stirring and minor amounts of dilution to form a uniform puree-like consistency as the feedstock. This contrasts strongly with the difficulty of forming a pumpable slurry for lignocellulosic feedstocks for hydrothermal processing [1]. For the CHG tests with the HTL aqueous byproduct, no feedstock preparation was required.

The pumping subsystem consists of a modified Isco 500D dual syringe pumps. Using the Isco pumps, the feeding rates were measured directly by the screw drive of the positive displacement syringe pump. The Isco pumps could pump either the algae slurries or the aqueous feed.

In the first two HTL tests, only the 1-liter continuous-flow stirred tank reactor (CSTR) was used. In the latter two tests the initial heat-up of the slurry was in an oil-heated tube-in-shell heat exchanger, which heated the feed to 133 °C. The final heat-up to reaction temperature was in the CSTR itself, which was reduced to a 400 ml vessel by insertion of a spacer. The reactor, an Inconel vessel equipped with internal stirring propellers, functioned as a back-mixed reactor and additional residence time was provided by a subsequently heated plug-flow portion of the reactor. This combination of CSTR and plug-flow was used in these tests as a result of conservative approach based on plugging problems experienced previously with a plug-flow only reactor system with lignocellulosic feedstocks. When the temperature in the initial preheater was maintained below 200 °C, there was no plugging detected with algal feedstocks.

In the CHG tests, the preheated feed from the CSTR passed through the solid separator as well as a sulfur stripping bed before entering the up-flow, fixed catalyst bed in the 1-liter tubular reactor. The catalyst used was ruthenium metal, 7.8% on a partially graphitized carbon extrudate.

As a result of the liquefaction chemistry, it was possible to separate the mineral matter from the liquid stream. In the HTL process, the organics in the algae were pyrolyzed and liquefied while certain inorganic components, such as calcium phosphates, formed and precipitated as solids. A vessel was placed in the process line following the reactor to capture and remove the solids at reaction conditions, temperature and pressure. The design of the separator was a combination settler, filtration unit wherein the solids fell to the bottom of a vessel and the liquids passed overhead through a filter to the reactor. The solids could be removed by batch from the bottom of the vessel as they built up over time. We found that by using this in-line system, a solid-free bio-oil product would more readily become separated from the water phase.

In the CHG configuration, the in-line filtration and sulfur scrubber system served to protect the catalyst bed in the tubular reactor from

mineral deposits and sulfur poisoning. The sulfur scrubbing component was nickel metal, 45% on a magnesium silicate tablet, with a 1% copper stabilizing agent [21].

In HTL mode, after exiting the solid separator, the products were routed to a dual liquid collecting system wherein the condensed liquids were collected at pressure. Periodically, the collection vessel was valved out and the flow was directed to the second collection vessel. In this way, the liquid product collection vessels could be alternately filled and drained. The gas byproduct was continuously vented overhead through a back-pressure regulator, metered, sampled for offline gas chromatography analysis, and then exhausted.

The product liquids were drained from the collectors into the sample holding jars. A lighter oil and heavier aqueous phase spontaneously formed and could be readily separated by cooling the sample and pouring the less viscous water from the oil. Elemental analysis was performed on the separated oil product to determine mass and elemental balances within the data windows. CHN, O, and S were analyzed by ASTM methods D5291, D5373, and D4239, respectively, and trace element analysis by ICP-OES as described previously [20]. The Total Acid Number (TAN) was done by D3339 and the moisture by D5530 (modified). The aqueous phase was analyzed for chemical oxygen demand (COD) and pH, with spot checks for ammonia and trace metals. Anions, including chloride, were measured by ion chromatography (IC) using a Dionex ICS 3000 IC as described previously [20].

Gas samples could be withdrawn manually from the vent line and analyzed every 30 to 60 min. In the HTL mode, the gaseous stream was mainly composed of CO₂ as well as water vapor. The gas product from CHG was primarily methane and carbon dioxide. Gas analysis was performed by gas chromatography (GC) as described earlier [20].

Actual startup of the hydrothermal liquefaction or catalytic hydrothermal gasification experiment usually required 2 to 4 h to bring the operating conditions to the desired levels. Subsequently, operating data were recorded and data windows were defined based on steady-state (or near steady-state) operating conditions.

2.2. Hydrotreating (HT) of algae biocrude products

The hydroprocessing experiments were undertaken in the bench-scale hydroprocessing system described in detail elsewhere [22]. That system included a fixed-bed catalytic reactor with required feeding and product recovery components. The bio-oil and hydrogen gas entered the top of the fixed catalyst bed and passed downward through the bed, assumed to be in a trickle-flow. After exiting the catalytic reactor, the products were cooled and collected in a dual cylinder sampling system, similar to the HTL system, with the uncondensable gases continuously metered and vented. The recovered liquid products were phase separated (oil from water products), weighed and sampled for further analysis. Manually recovered gas samples were analyzed by gas chromatography, as described before [22].

In the first experiment with HTL biocrude from Solix LEA, the temperature in the top 1/4th of the reactor was lower, 125–170 °C, with a liquid hourly space velocity (LHSV) of 0.66 l of bio-oil per liter of catalyst bed per hour. After low-temperature processing, the partially hydrotreated bio-oil then proceeded directly into the high-temperature stage for subsequent catalytic hydroprocessing typically at 405 °C and 0.18 LHSV for an overall LHSV of 0.14. In the latter three HT tests, a single temperature stage was demonstrated at 405 °C with a higher LHSV of 0.20. The hydroprocessing catalyst

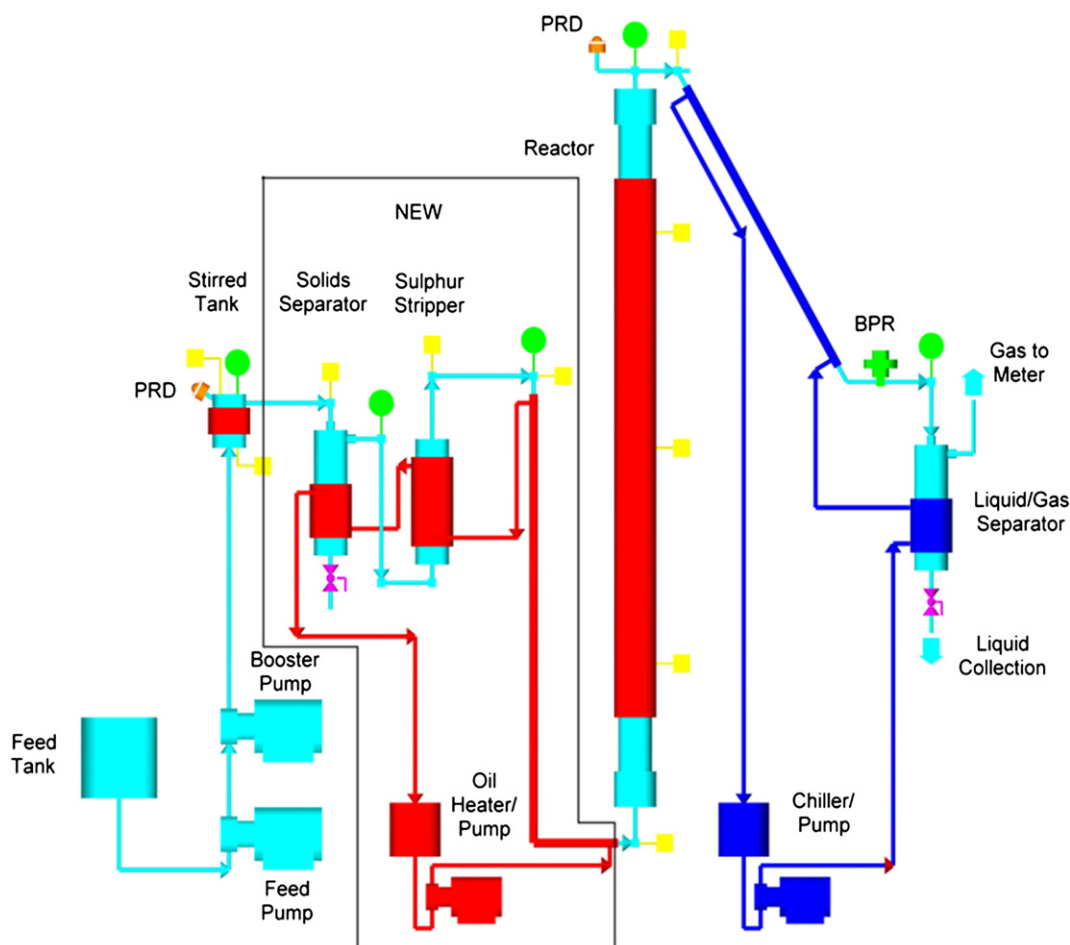


Fig. 1. Bench-scale, continuous-flow system in original CHG configuration.

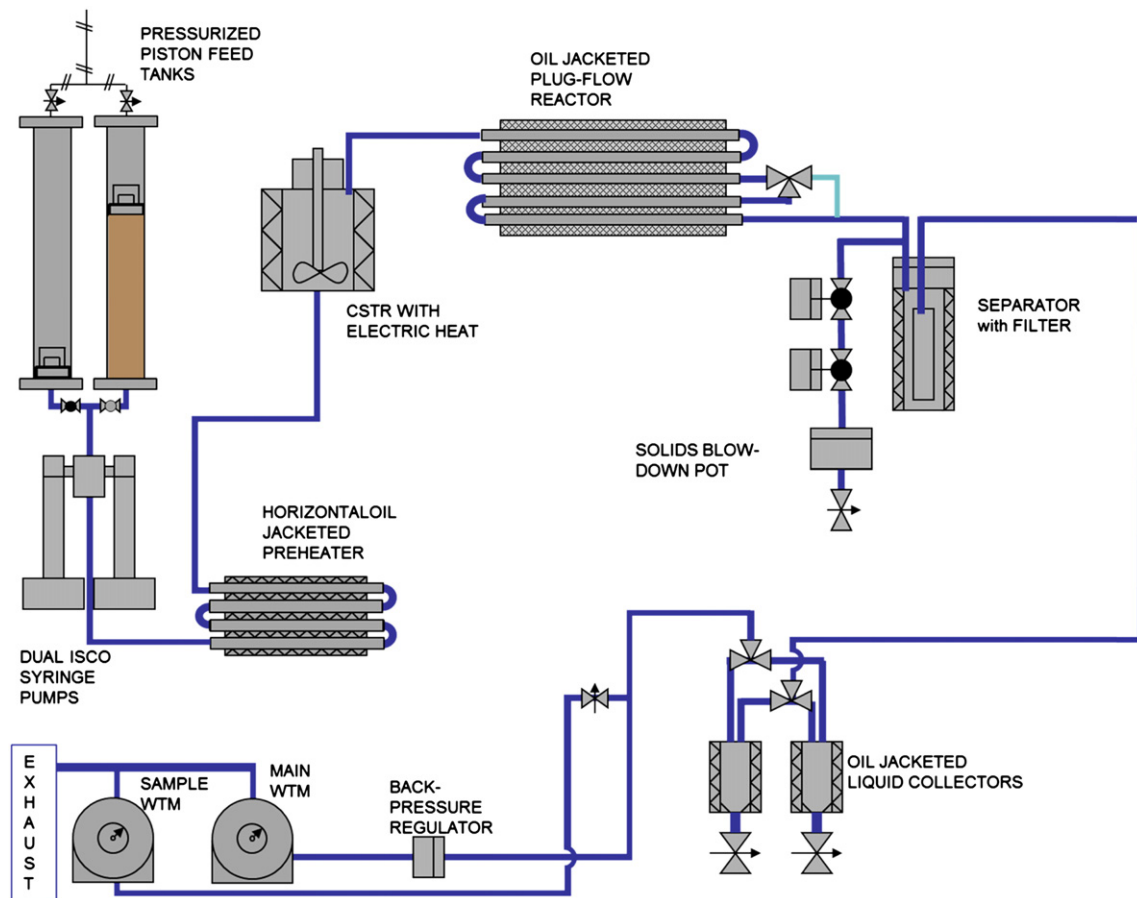


Fig. 2. Process flow configuration for hydrothermal liquefaction.

in both stages was a molybdenum sulfide catalyst with cobalt promotion on a fluorinated-alumina support (KF-1001, 4% Co, 15% Mo, 1/16 in diameter). Both stages were operated at the same pressure of 13.6 MPa, nominally, with a hydrogen flow in great excess of the process requirement. The catalyst bed was sulfided prior to the test by processing a solution of di-*tert*-butyl disulfide (DTBDS) in decane under hydrogen. The HTL biocrude contained enough sulfur in the feed that no additional sulfur was added.

3. Results and discussion

The testing discussed here produced initial results for continuous-flow processing of wet algae feedstocks in the bench-scale reactor. The HTL process was operated at nominally 20 MPa and 350 °C using dewatered algae slurries at 17–35 wt.% dry solids, as shown in Fig. 3.

The CHG process similarly was operated in a continuous-flow mode at the same conditions using the HTL aqueous byproduct as the feedstock. The HT process was also performed in a bench-scale continuous-flow reactor operated nominally at 14 MPa with a temperature bed ranging from 125 to 405 °C in one case or just at 405 °C in the later tests, using the algae HTL biocrude as the feedstock. The products are presented in photographs in Fig. 4.

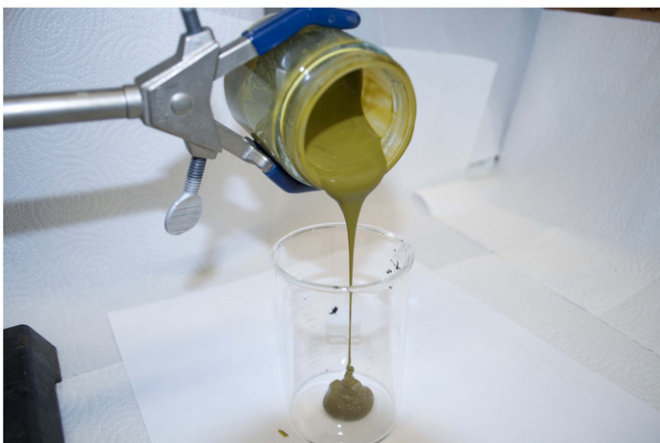


Fig. 3. Algae slurry feedstock for hydrothermal liquefaction.

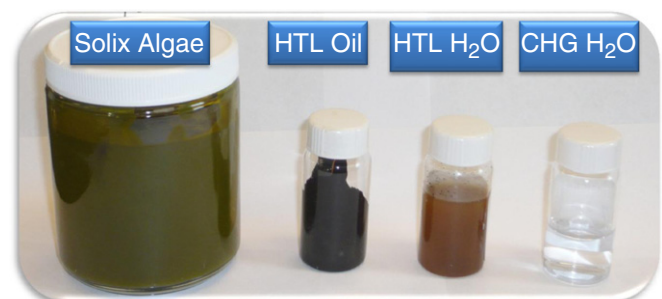


Fig. 4. Algae slurry feedstock and hydrothermal processing products.

Table 1
Process data for algae processing.

	HTL	HT	CHG
Temperature, °C	344–362	405–414	350–353
Pressure, psig	2966–3020	1931–1974	2940–3015
LHSV, L/L/h	1.5–2.2	0.14–0.20	1.49–2.00
H ₂ consumption, L/L	NA	298–501	NA
Carbon gasification, %	1.8–5.1	7.3–9.1	100.2–104.4
Carbon to aqueous, %	15.2–43.9	0.2–0.4	1.2–0.2
Carbon loss in solid, %	0.1–1.7	NA	0.0
Carbon in oil, %	81.8–50.3	90.5–92.0	NA

A total of four HTL tests were performed and the produced biocrude products were hydrotreated in 3 of the cases. Three of the aqueous byproduct streams were gasified. The range of process conditions tested in the three processes is given in Table 1. Liquid hourly space velocity (LHSV) is calculated based on feedstock volume at ambient conditions versus the volume of the reactor at reaction conditions on an hourly basis. The hydrotreating (HT) process has much slower kinetics and thus is performed at a much lower space velocity. Hydrogen consumption is only relevant to HT; hydrogen is a minor product in the hydrothermal processes. The carbon distribution in the product slate is also given in Table 1.

3.1. Hydrothermal liquefaction

The four algae tested were the Lipid Extracted Algae (LEA) from Solix (solixbiofuels.com), the NB238 product from the Pecos large scale cultivation test bed (algaeorfuel.agrilife.org) operated by Texas A&M University, and two algae from Cellana, produced using their patented ALDUO™ system (cellana.com), one harvested after high growth operation (low lipid = AGLL) and one harvested after stressed, low-growth conditions (high lipid = AGHL). All four algae are *Nannochloropsis sp.* and were provided by the NAABB partners. Details of the cultivation and harvesting systems are considered proprietary but some general information is available on their websites. The feedstock analyses are provided in Table 2. The most abundant trace metals were sodium, iron and potassium. These low-ash algae resulted in little mineral precipitation and no mineral blowdown was required during the process tests that lasted between 8.75 h and 10.2 h on 5 different days of operation. The first two tests were performed with the original 1-liter CSTR, while the second two tests were performed with a spacer in place in the CSTR to reduce the reactor volume and increase the space velocity. Although the mineral separator following the reactor is maintained at near reaction conditions, its volume is not included in the LHSV calculation for these experiments.

As seen in Table 1, the biocrude product is typically where most of the carbon is recovered. The process products and yields for hydrothermal

Table 2
HTL feedstocks analyses.

	Solix LEA	NB238	Cellana AGLL	Cellana AGHL
Carbon, wt.% dry	49.7	47.6	52.0	51.5
Hydrogen, wt.% dry	7.1	6.6	7.5	7.3
Oxygen, wt.% dry	26.7	21.7	22.4	22.4
Nitrogen, wt.% dry	5.8	5.5	4.8	4.5
Sulfur, wt.% dry	1.0	1.6	0.62	0.63
Ash, wt.%	11.1	9.2	12.9	12.3
Density, g/ml@40 °C	1.05	1.04	1.06	1.09
pH	nd	4.1	6.0	5.05
Chemical oxygen demand, ppm	265,380	226,830	580,333	590,500
Dry solid content, wt.%	17.00	19.94	34.42	32.93
Feed processing rate, l/h	1.50	1.49	1.50	1.49
LHSV, L feed/L reactor/h	1.50	1.49	2.23	2.21

nd = not determined.

Table 3
HTL products.

	Solix LEA	NB238	Cellana LL	Cellana HL
Biocrude				
Yield, wt.% DAF	53.2	38	60.8	63.6
Carbon, wt.% dry	79.2	78.6	77.0	77.6
Hydrogen, wt.% dry	10.0	10.4	10.4	10.6
Oxygen, wt.% dry	5.7	5.3	8.0	7.2
Nitrogen, wt.% dry	4.7	4.2	4.2	4.0
Sulfur, wt.% dry	0.5	0.5	0.3	0.3
Moisture, wt.%	7.8	5.2	2.8	4.5
Density, g/ml@40 °C	0.946	0.96	0.943	0.953
Viscosity, cSt@40 °C	205	114	354	355
TAN, mg KOH/g	nd	59	68	74
Aqueous				
Carbon, wt.%	2.5	1.8	3.2	3.7
Nitrogen, wt.%	0.7	0.5	1.1	1.0
pH	7.72	7.6	7.50	7.48
COD, mg/kg	82,000	59,900	95,600	125,500
Gas				
Carbon dioxide, vol.%	47	36	42	46
Hydrogen, vol.%	0	0	0	0
Carbon monoxide, vol.%	0	0	0	0
Methane, vol.%	3	11	13	4
Ethane, vol.%	1	2	1	1
Ammonia, vol.% (tentative)	49	52	44	49

nd = not determined.

DAF = dry, ash-free basis.

liquefaction are given in Table 3. The HTL biocrude products from algae are viscous oils with much of the oxygen removed in all four cases, even though a different reactor configuration was used for the first two tests.

Compared to a HTL biocrude from lignocellulosics [5], the algae biocrude is lower in density, contains less dissolved water and has a lower acid content (TAN). On the other hand it is more viscous at room temperature, and has higher nitrogen and sulfur contents. Although the aqueous phase from HTL contains a much lower level of carbon, it amounts to a significant fraction of the carbon in the feedstock. The nitrogen fraction in the aqueous phase also amounts to about half of the nitrogen in the algae. The aqueous phase has a nearly neutral pH due to the dissolved ammonia and alkali available to neutralize the residual organic acids, represented by the substantial COD. The gas product is mostly carbon dioxide, but a large fraction of ammonia has been tentatively found, but its calibration is suspect, and the number reported may be high by as much as 50%. The levels of hydrogen and carbon monoxide were below the level of detection.

GC–MS analysis of the NB238 HTL oil product showed an interesting collection of components suggesting the production of the oil from both the lipids as well as the carbohydrates and proteins in the algae. The chromatograph (which only represents the volatile portion of the product) showed a complex mixture of light compounds through a range of aromatic hydrocarbons and phenolic compounds. There were also heterocyclic compounds containing nitrogen (indoles) and cyclopentenones. In the higher molecular weight range, there was a collection of fatty acids and amides as well as the straight chain alkanes in the C15 to C22 range. These results compare favorably with Brown et al. [17a] who also reported these products in batch tests performed with *Nannochloropsis* at 350 °C, but who also showed a dramatic change in product composition to polycyclic aromatics when processing at a higher temperature of 500 °C. Our results were only semi-quantitatively determined by total ion count. The chromatograph is shown in Fig. 5. The initial large unlabeled peak is a solvent.

The aqueous and solid byproducts recovered from HTL could provide a mechanism for recovering important nutrients, such as P and N, which could be recycled to the algae growth medium. Attempts to determine the elemental balance of these components using less than optimal analytical methods have given inconsistent results, thus far. Table 4 gives

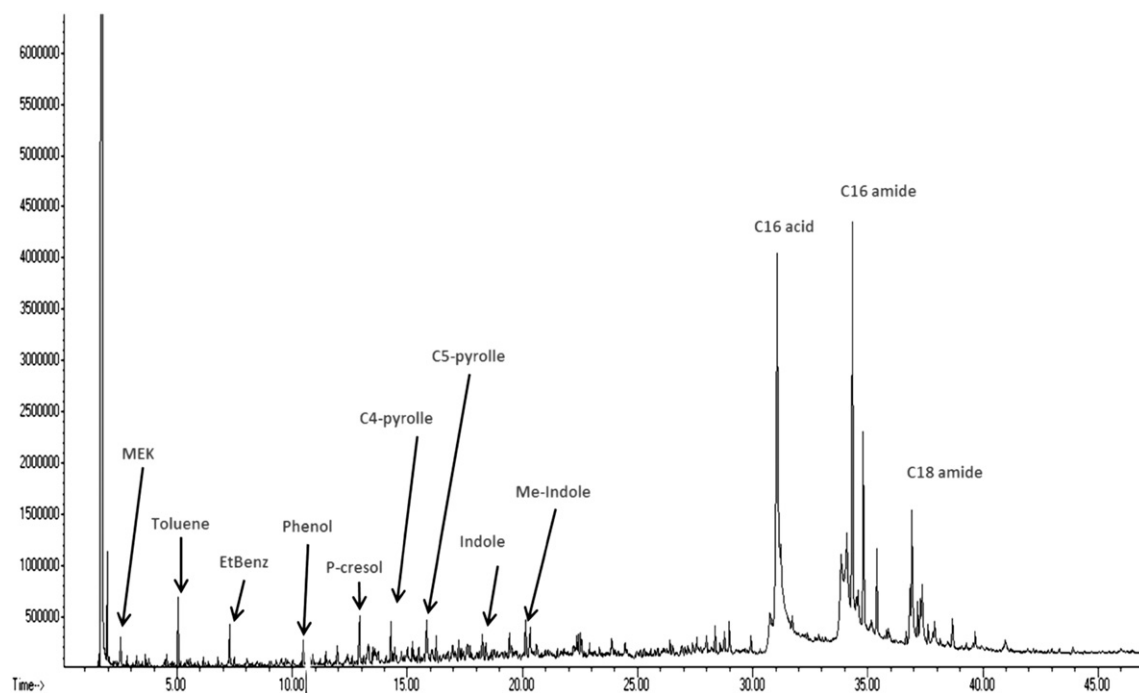


Fig. 5. Total ion chromatograph of algae HTL biocrude in methanol.

the data for the NB238 HTL test, listing the amounts of material and concentrations to determine actual amounts of elements. The data suggests that the phosphorus accounting is well short of the total in the feed. The major portion recovered has been in the precipitated solids. The small recovery of solids suggests that incomplete recovery of the solids is the shortcoming and that better product recovery will confirm that almost all of the P can be recovered in the separated solids. Release of the P into a soluble form through acid dissolution should be feasible since that is the method for sample preparation for the analysis.

The data for nitrogen provided a closer balance of 86% being accounted for. In this case half of the nitrogen would be available for direct recycling as dissolved ammonium in the aqueous byproduct as was evaluated earlier by Jena et al. [16b]. However, should the organic components prove toxic, then the further treatment of the aqueous by CHG would be indicated as a means to remove the organic and recover the energy value as a fuel gas. The dissolved organics have been identified by liquid chromatography, to a limited degree, and the major components found include methanol, ethanol, glycerol, acetic and glycolic acids. The next most important nitrogen recycle stream appeared to be the gas product, which contained about one third of the nitrogen as

ammonia gas. This is a new development, which others have not reported, mostly because they did not have an ammonia gas analysis capability. The gas analysis was only approximate and will require further detailed analysis to confirm. In addition, the depressurization of the high-pressure liquid collecting system (pressurized with nitrogen) provided a mechanism for unaccounted ammonia to move out of the aqueous solution. Development of an alternate collection method may allow the ammonia to be maintained as dissolved ammonium in the aqueous byproduct. The amount of nitrogen that reports to the oil product in this case is a small fraction. There is a report in the literature [17c] that suggests that the distribution of the nitrogen between the oil and aqueous is dependent on the HTL processing conditions, particularly temperature, and our results may be indicative of only one case.

Data for the AGLL and AGHL tests provide similar information, as shown in Table 5. The phosphorus analyses were not completed except the very low level of P remaining in the aqueous byproduct was confirmed at only 14 and 12 ppm in the tests with AGLL and the AGHL, respectively. The nitrogen balances both over-reported the nitrogen in the products; however, the results are similar in showing not quite half of the N remaining in the aqueous phase and the oil portion of the nitrogen is higher, about a third, while the gas portion is lower, somewhat less than a third.

Table 4
Nutrient balance for NB238 HTL.

Component	Concentration	Amount	Portion of feed recovered	Selectivity of byproduct
<i>Phosphorus balance</i>				
Feed, 307.3 g/h	2802 ppm	0.861 g/h	27%	
Solid, 2.05 g/h	84,570 ppm	0.173 g/h	20%	75%
Aqueous, 1498.6 g/h	15 ppm	0.022 g/h	3%	10%
Oil, 42.8 g/h	825 ppm	0.035 g/h	4%	15%
<i>Nitrogen balance</i>				
Feed, 307.3 g/h	5.52 wt.%	16.96 g/h	86%	
Solid, 2.05 g/h	0.97 wt.%	0.02 g/h	0.1%	
Aqueous, 1498.6 g/h	0.54 wt.%	8.09 g/h	48%	56%
Oil, 42.8 g/h	3.88 wt.%	1.66 g/h	10%	11%
gas, 12.8 L/h	52 vol.%	4.72 g/h	28%	33%

Table 5
Nitrogen balance for AGLL/AGHL.

Nitrogen Balance				
Component	Concentration	Amount, g/h	Portion of feed recovered	Selectivity of byproduct
Feed, 550.4/536.4 g/h	4.83/4.48 wt.%	26.58/24.03	126%/133%	
Solid, 2.89/1.85 g/h	2.38/0.71 wt.%	0.07/0.01	0.3%/0.04%	0.2%/0.03%
Aqueous, 1236.7/1184.5 g/h	1.10/0.95 wt.%	13.60/11.25	51%/47%	41%/35%
Oil, 291.3/304.9 g/h	3.99/3.73 wt.%	11.62/11.37	44%/47%	35%/35%
Gas, 25.9/27.2 L/h	44/49% vol.%	8.07/9.44	30%/39%	24%/29%

Table 6
HTL biocrude hydrotreating product compositions.

	Solix LEA	NB238	Cellana LL	Cellana HL
<i>HT bio-oil</i>				
yield, wt% DAF	79.5	84.4	84.6	80.7
carbon, wt% dry	85.0	85.4	84.4	84.2
hydrogen, wt% dry	14.2	13.3	13.5	14.0
oxygen, wt% dry	0.8	1.2	1.8	1.7
nitrogen, wt% dry	<0.05	0.16	0.25	0.07
sulfur, ppm dry	3.7	<50	<50	<50
moisture, wt%	0.16	0.33	0.05	0.03
density, g/ml@40C	0.80	0.783	0.768	0.787
viscosity, cSt@40C	NA	2.5	4.5	4.5
TAN, g KOH/L	<0.01	0.2	<0.1	0.1
<i>Aqueous</i>				
carbon, wt%	1.4	0.7	0.8	0.8
nitrogen, wt%	11.9	12.0	12.8	7.3
pH	NA	10.92	10.76	10.27
COD, mg/kg	NA	9600	11,250	5400
<i>Gas, H₂ free basis</i>				
carbon dioxide, vol%	0	0.8	0.9	2
hydrogen, vol%	–	–	–	–
carbon monoxide, vol%	0	0.9	3	2
methane, vol%	57	31	36	48
ethane, vol%	30	19	15	21
ammonia, vol%	NA	42	33	NA
higher HC, vol%	13 ^a	7	12	27 ^a

DAF = dry, ash-free basis.

^a Not adjusted for presence of ammonia.

Of the other algae HTL work in the literature, there is only one group that mentions ammonia analysis in their gas products [12a]. Others [15,17] have reported nitrogen or in other cases have been limited to only non-nitrogen containing gases [16c], while yet others do not report gas analysis or quantify recovery, except by difference [14]. In the attempt by Ross et al. 2010 [12a], analysis of gaseous nitrogen containing compounds are discussed, but in the end the quantitation of the yield was not done, and although ammonia was reported at 60 to 140 ppm by FTIR, the nitrogen containing gaseous fraction was determined by difference. Therefore our attempt at a nitrogen balance is the first actual complete attempt.

Analysis of the aqueous byproduct by ICP identified the major soluble components as expected—sodium (13,000 to 16,000 ppm),

potassium (4600–5000 ppm) and sulfur (900 to 1200 ppm) with only a little silicon (67 to 79 ppm) and the trace of phosphorus mentioned above. Other elements were present at a level below the level of detection, 8 ppm. Nickel is included in this list of other elements and based on this low level and the expected further dilution upon recycle may be considered a non-issue based on results of culture toxicity done elsewhere [4b].

Further analysis of the HTL aqueous byproduct by ion chromatograph showed for the NB238 feedstock test that both chloride and bromide were present, 90 to 184 ppm and 39 to 83 ppm of chloride and bromide, respectively. In the tests of the AGLL and AGHL feedstocks, grown in salt water, the chloride in the aqueous byproduct was much higher at 28,000 to 30,000 ppm. A cursory inspection of the reactor tubes following the tests found no signs of corrosion in the reactor system, even at the high chloride concentration and the high temperature. Apparently, the third important factor, pH, which was near neutral in these process tests, due to the large presence of both ammonium and alkali, was the overriding factor which limited corrosion.

3.2. HTL biocrude hydrotreating

Table 6 gives the products and yields from the hydrotreating (HT) of the HTL biocrude. Catalytic hydrotreatment of the oil produced an almost oxygen free hydrocarbon blend with a slightly higher residual oxygen content in the later three tests where a single hydrotreating catalyst bed was used at a higher space velocity. HT resulted in desulfurization and denitrogenation down to nearly immeasurably low levels, which correlate with the deoxygenation level in that they are lower in the first test, which was performed at more severe conditions. It is counter-intuitive that the density is higher for the more severely hydrotreated product oil. TAN was reduced to below the level of detection due to oxygen removal, but the effect may also result from ammonium neutralization of the remaining acids. The viscosity and density both correlate with the high H to C atomic ratio 1.98 at the more severe conditions to 1.85 in the later tests. With such low remaining oxygen content, the solubility of the oil in water was quite low and the carbon content in the aqueous reflects that. The nitrogen content of the aqueous was relatively high, suggesting the presence of a substantial amount of ammonium. The gas products were mostly hydrocarbon, with a tentative identification of ammonia, with little carbon oxides recovered.

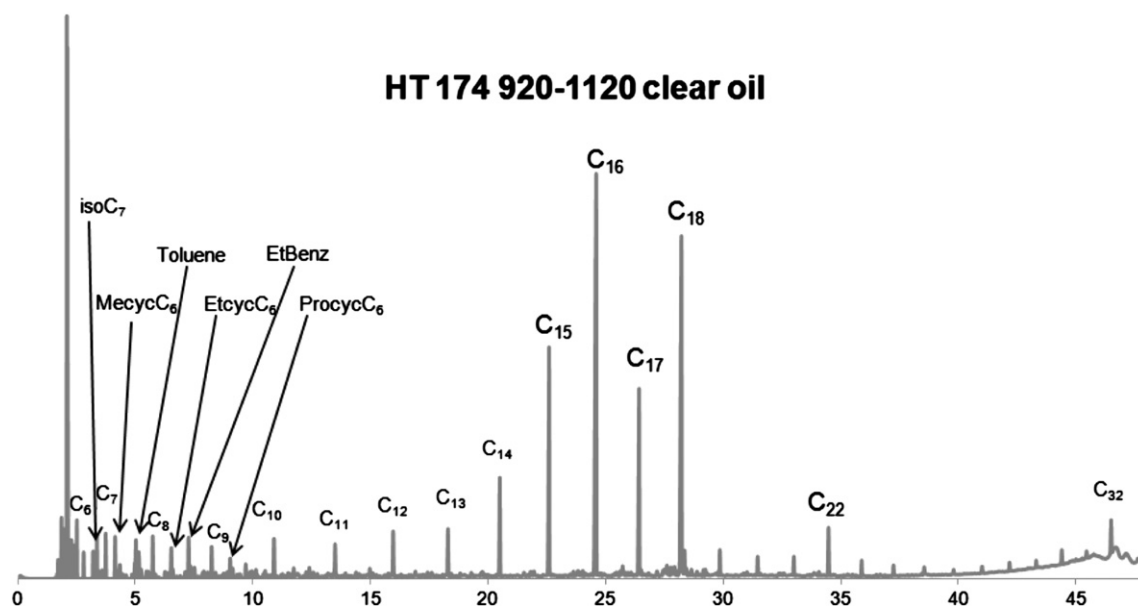


Fig. 6. Total ion chromatograph of hydrotreated algae HTL biocrude.

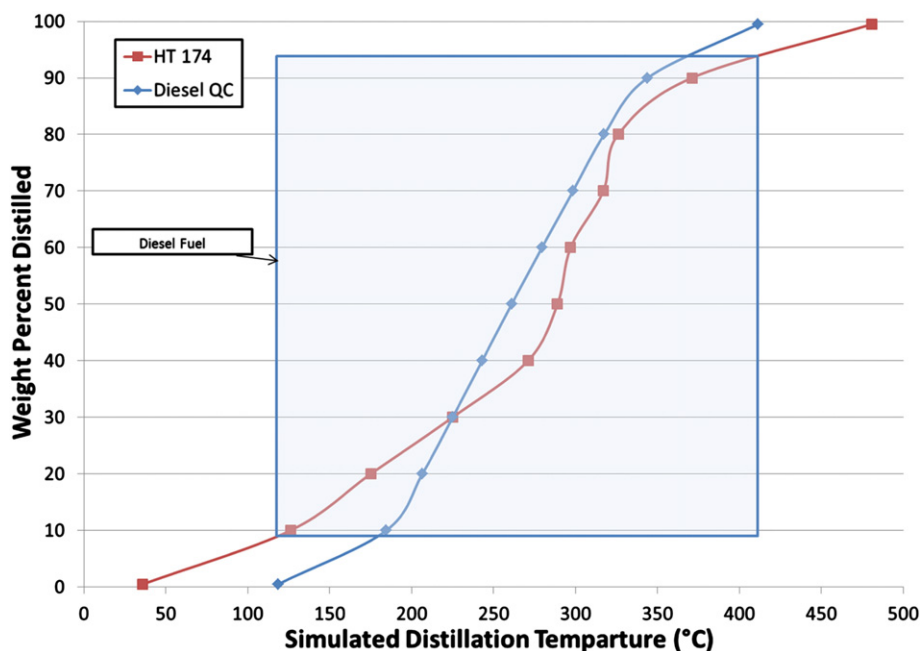


Fig. 7. Simulated distillation curve for hydrotreated algae HTL biocrude.

The HT oil products were analyzed for composition and properties. Analysis by GC–MS shows that the volatile components are an interesting mixture of light cyclic hydrocarbons, both aromatic and naphthenic, which would result from biomass liquefaction, as well as longer chain alkanes suggesting lipid structure transformation. Fig. 6 shows the total ion chromatograph.

Again, the initial large unlabeled peak is a solvent. Our results contrast with those of Duan and Savage [23] who reported hydrotreatment of *Nannochloropsis* HTL biocrude in a batch reactor using a platinum-on-carbon catalyst and in which they did not achieve the high level of heteroatom removal reported here.

In the case of this hydrotreated product, the chromatograph is representative of the bulk of the product. As shown by D2887 simulated distillation, the product falls primarily in the diesel range, defined as less than 10% boiling below 180 °C and less than 10% boiling above 350 °C, (see Fig. 7). Further analysis showed that all detectible components were less than C₄₀. Based on the definition of diesel, about 80–85% of this hydrotreated HTL biocrude would be blendable into the diesel pool.

A recent report describes the use in a batch reactor of an acidic cracking catalyst in the presence of hydrogen for upgrading algae HTL biocrude [24]. Using higher temperatures of 450 and 500 °C, deoxygenation similar to that reported here was reported. Yet, the use of oxygen “by difference” as opposed to actual measurement and the report of better deoxygenation in the absence of a catalyst, cast doubt on the results. The more relevant comparison to Duan and Savage’s batch reactor results [23] also differs from common hydrotreating by the use of a precious metal catalyst versus the typical promoted sulfided–molybdenum system. The difference in catalyst is the likely explanation for the higher oxygen contents reported in their final product composition. However, comparisons of continuous-flow systems to batch systems are difficult as the products from the batch are often equilibrium limited, even assuming that they are not hydrogen limited, stoichiometrically.

3.3. HTL aqueous gasification

The CHG of the HTL aqueous byproduct resulted in nearly complete gasification of the remaining organic components as shown by the results in Table 7. COD of the water was reduced by 98.8 to 99.8%. The

typical high methane and carbon dioxide gas was produced with little hydrogen or higher hydrocarbons. Ammonia was noted among the product gases. The results presented in Table 7 are with times on stream ranging from 8.1 to 42.2 h of operation. The same catalyst composition was used for all the tests, a 7.8 wt.% ruthenium metal on a partially graphitized carbon extrudate. The activity and stability of this catalyst have been demonstrated previously [25].

Nutrient balance around the CHG of the HTL aqueous was focused on the nitrogen and sulfur components as there was essentially no phosphorus in the aqueous stream following the high-temperature mineral separation step included with HTL. Nitrogen in the CHG feedstock was recovered for the most part in the aqueous effluent. As shown in Table 8, the concentrations of total nitrogen in the feedstocks were accounted for in large part by the dissolved ammonium. The concentration of dissolved ammonium actually increased slightly through the CHG step as some water was used up in the gasification reactions.

There was residual sulfate in the HTL aqueous byproduct which was used as CHG feedstock. In order to precipitate this sulfate before it could enter the catalyst bed and poison the catalyst, calcium hydroxide was added in stoichiometric excess (5 g/l), so that calcium sulfate would precipitate. No significant amount of insoluble solids was recovered in either the AGLL or the AGHL test, except for a thin film of deposit in the solid separator. However, after the test it was found that the feed

Table 7
Product compositions from CHG of HTL aqueous byproduct.

	Solix	Cellana LL	Cellana HL
<i>Aqueous</i>			
Nitrogen, ppm (NH ₃) ppm	nd	9290	9250
pH	7.85	7.58	7.52
COD, mg/kg	165	971	1042
<i>Gas</i>			
Carbon dioxide, vol.%	33	28	33
Hydrogen, vol.%	2	2	2
Carbon monoxide, vol.%	0	0	0
Methane, vol.%	59	66	62
Ethane, vol.%	1	0.6	0.1
Ammonia, vol.%	5	6	5

nd = not determined.

Table 8
Nutrient balance for CHG.

Nitrogen balance			Sulfur balance	
component	N, wt.%	NH ₃ -N ppm	S, wt.%	SO ₄ ²⁻
AGLL feed	0.86	7587	0.116	4700 ppm
AGLL effluent	NA	9293	8–21 ppm	4–8 ppm
AGHL feed	0.80	6710	0.095	4260 ppm
AGHL effluent	NA	9250	4–8 ppm	

Table 9
Trace element balance for CHG.

component	Na ppm	K ppm	Ca ^a ppm	S ppm	Si ppm	Mg ppm	Fe ppm
AGLL feed	9500	3300	1800	780	94	14	<8
AGLL effluent	9300	3800	2	7	20	<0.8	<0.8
AGHL feed	8900	3800	4800	790	85	30	10
AGHL effluent	11,000	3900	2	12	22	<0.8	<0.8

^a Ca added to HTL aqueous byproduct before feeding to CHG test.

tank contained an indeterminate amount of precipitate, which analysis suggested it to be calcium sulfate. As shown in Table 8, the sulfur in the feedstock (by direct thermal analysis D4239) is represented in excess by sulfate determined by IC. There is almost no sulfate left in the effluent of CHG, meaning that it had precipitated somewhere in the process, apparently in the feed tank. Similarly, the Ca level in the CHG effluent was very low, 1–3 ppm.

Other trace elements in the aqueous stream were of interest. The analysis by ICP-OES provided the data presented in Table 9. We found that alkali metals, Na and K, were present and remained dissolved in the aqueous, except for some small amount recovered with the calcium sulfate from the solid separator after the test. The Ca and S were reduced to low levels in the effluent as described above, as were the Si, Mg and Fe. No evidence of Ru migration from the catalyst bed by dissolution was found in these tests as it was below the level of detection, <0.8 ppm, throughout.

Chloride is another significant factor as the algae were grown in a marine environment. The feedstock for CHG was measured at around 30,000 ppm Cl while the effluent was measured at only 20,000 ppm. This incomplete chloride recovery should be addressed in future work including a more careful chlorine balance. As well, a detailed corrosion assessment within the reactor systems should be undertaken in light of the presence of substantial chlorine. As reported above in the discussion of the HTL step, no evidence of corrosion by visual inspection was found in these limited tests, although such an analysis might not detect initial stages of stress corrosion cracking as might be caused by chloride. Chloride stress corrosion cracking may not be effective in this environment due to the near neutral pH and lack of free oxygen.

3.4. Overall process considerations and modeling

These process data have been used for development of a process model upon which an economic assessment of the process was made

[26]. That study concluded that the high capital cost could be ameliorated by operation of the process at larger scale. The largest uncertainty is the cost of the algae feedstock. As shown in Fig. 8, the overall yield of liquid hydrocarbon fuel on a dry basis is substantial, over 40% of the algal mass. The approximate residence time for HTL is provided. Its calculation based on the LHSV is not straight-forward because of the large change in volumes of the reactants at the high-pressure reaction condition and temperature, which is near (but maintained below) the critical point of water.

Others have attempted life cycle analysis of the concept [27]. In comparison to direct lipid extraction methods, the HTL-based process has nearly twice the oil yield but the recovery and recycle of the nutrients was identified as a key subject to address in future research. The overall process from algae to fuel products is depicted in Fig. 9.

4. Conclusions

The algae feedstocks were reliably processed even with high slurry concentrations of up to 35 wt.% dry solids in a high-pressure, continuous-flow system. The high yield of a biocrude product from whole algae achieved in this readily scaleable processing system and the analysis of the biocrude content suggest that it consisted of both lipid-derived alkane products and heterocyclics derived from the other biomass components. Catalytic hydrotreating of the biocrude demonstrated the removal of the heteroatoms from the biocrude and the formation of the light sweet blending stock which should be valuable for blending into petroleum refineries for the production of renewable fuels. High methane content product gas was produced by catalytic hydrothermal gasification of the HTL aqueous byproduct. The removal of the organic material should facilitate the recycle and reuse of the dissolved nutrients (N and K) in the aqueous stream.

Hydrothermal processing of biomass to liquid and gaseous fuels requires expanded process development to take the technology to a scale for industrial demonstration. Technical challenges associated with hydrothermal processing of biomass include the issues associated with defining the properties of the byproducts, which are highly dependent on the feedstock composition; optimization of the liquefaction and gasification process variables; and demonstrating the effectiveness of separation techniques to remove precipitated nutrients (primarily phosphate, but also sulfate) before catalyst poisoning. Recycle of nutrients from the recovered byproducts (P in solids and N, K, & C in aqueous) is a potential area for process cost savings and improved sustainability.

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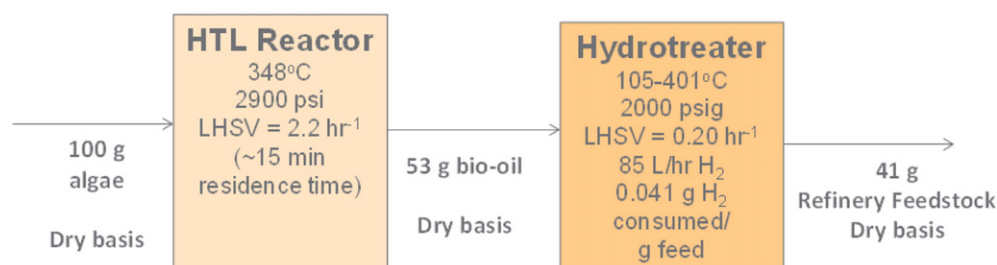
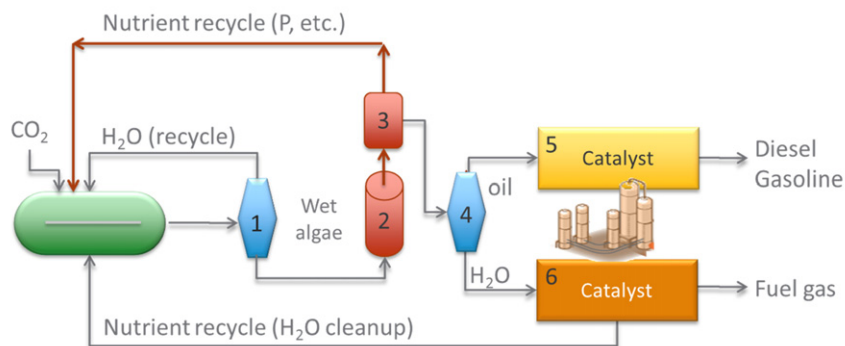


Fig. 8. Process flow for liquid fuels from algae by hydrothermal processing.



1. algae de-watered from 0.6 g/L to 200 gg/L
2. hydrothermal liquefaction
3. solid precipitate separation for clean bio-oil production and phosphate capture
4. oil/water phase separate
5. oil hydrotreater to produce hydrocarbons—diesel/gasoline
6. aqueous phase carbon is catalytically converted to fuel gas and nutrients recycled (N, K, some CO₂, etc)

Fig. 9. Process scheme utilizing algae growth and hydrothermal processing for fuels.

the NAABB (also funded by BETO) who provided the algae feedstocks for our tests.

References

- [1] D.C. Elliott, Hydrothermal processing, in: R.C. Brown (Ed.), *Thermochemical Processing of Biomass: Conversion into Fuels, Chemicals and Power*, John Wiley & Sons, Ltd., Chichester, UK, 2011, pp. 200–231.
- [2] M.C. Chow, W.R. Jackson, A.L. Chaffee, M. Marshall, Thermal treatment of algae for production of biofuel, *Energy Fuel* 27 (2013) 1926–1950.
- [3] D.C. Elliott, T.R. Hart, G.G. Neuenschwander, Chemical processing in high-pressure aqueous environments. 9. Process development for catalytic gasification of algae feedstocks, *Ind. Eng. Chem. Res.* 51 (2012) 10768–10777.
- [4] (a) S. Stucki, F. Vogel, C. Ludwig, A.G. Haiduc, M. Brandenberger, Catalytic gasification of algae in supercritical water for biofuel production and carbon capture, *Energy Environ. Sci.* 2 (2009) 535–541; (b) A.G. Haiduc, M. Brandenberger, S. Suquet, F. Vogel, R. Bernier-Latmani, C. Ludwig, SunChem: An integrated process for the hydrothermal production of methane from microalgae and CO₂ mitigation, *J. Appl. Phycol.* 21 (2009) 529–541.
- [5] NABC HTL highlights, (last accessed May 2, 2013), http://www.nabcprojects.org/pdfs/htl_stage_2_developments_102212.pdf http://www.nabcprojects.org/pdfs/hydrothermal_liquefaction_results_stage_i_extension.pdf http://www.nabcprojects.org/pdfs/hydrothermal_liquefaction_route_to_improved_bio-oils.pdf.
- [6] D.C. Elliott, G.G. Neuenschwander, T.R. Hart, L.J. Rotness, A.H. Zacher, S.L. McDonald, G. Dassor, K.A. Fjare, B.C. Dunn, Hydrothermal liquefaction of agricultural and biorefinery residues: final CRADA Report #PNNL/277, PNNL-19453, Pacific Northwest National Laboratory, Richland, Washington, 2010.
- [7] R.S. Sayre, *Bioscience* 60 (2010) 722–727.
- [8] D.L. Barreiro, W. Prins, F. Ronsse, W. Brilman, Hydrothermal liquefaction (HTL) of microalgae for biofuel production: state of the art review and future prospects, *Biomass Bioenergy* 53 (2013) 113–127.
- [9] S.S. Toor, L. Rosendahl, A. Rudolf, Hydrothermal liquefaction of biomass: a review of subcritical water technologies, *Energy* 36 (2011) 2328–2342.
- [10] Y. Dote, S. Sawayama, S. Inoue, T. Minowa, S.-Y. Yokoyama, Recovery of liquid fuel from hydrocarbon-rich microalgae by thermochemical liquefaction, *Fuel* 73 (1994) 1855–1857.
- [11] T. Minowa, S.-Y. Yokoyama, M. Kishimoto, T. Okakura, Oil production from algal cells of *Dunaliella tertiolecta* by direct thermochemical liquefaction, *Fuel* 74 (1995) 1735–1738.
- [12] (a) A.B. Ross, P. Biller, M.L. Kubacki, H. Li, A. Lea-Langton, J.M. Jones, Hydrothermal processing of microalgae using alkali and organic acids, *Fuel* 89 (2010) 2234–2243; (b) P. Biller, A.B. Ross, Potential yields and properties of oil from the hydrothermal liquefaction of microalgae with different biochemical content, *Bioresour. Technol.* 102 (2011) 215–225; (c) P. Biller, A.B. Ross, S.C. Skill, A. Lea-Langton, B. Balasundaram, C. Hall, R. Riley, C.A. Lewellyn, Nutrient recycling of aqueous phase for microalgae cultivation from the hydrothermal liquefaction process, *Algal Res.* 1 (2012) 70–76.
- [13] S. Zou, Y. Wu, M. Yang, C. Li, J. Tong, Bio-oil production from sub-and supercritical water liquefaction of microalgae *Dunaliella tertiolecta* and related properties, *Energy Environ. Sci.* 3 (2010) 1073–1078.
- [14] (a) L.G. Alba, C. Torri, C. Samori, J. van der Spek, D. Fabbri, S.R.A. Kersten, D.W.F. Brilman, Hydrothermal treatment (HTT) of microalgae: evaluation of the process as conversion method in an algae biorefinery concept, *Energy Fuel* 26 (2012) 642–657; (b) C. Torri, L.G. Alba, C. Samori, D. Fabbri, D.W.F. Brilman, Hydrothermal treatment (HTT) of microalgae: detailed molecular characterization of HTT oil in view of HTT mechanism elucidation, *Energy Fuel* 26 (2012) 658–671.
- [15] G. Yu, Y. Zhang, L. Schideman, T.L. Funk, Z. Wang, Hydrothermal liquefaction of low lipid content microalgae into bio-crude oil, *Trans. ASABE* 54 (2011) 239–246.
- [16] (a) U. Jena, K.C. Das, J.R. Kastner, Effect of operating conditions of thermochemical liquefaction on biocrude production from *Spirulina platensis*, *Bioresour. Technol.* 102 (2011) 6221–6229; (b) U. Jena, N. Vaidyanathan, S. Chinnasamy, K.C. Das, Evaluation of microalgae cultivation using recovered aqueous coproduct from thermochemical liquefaction of algal biomass, *Bioresour. Technol.* 102 (2011) 3380–3387; (c) U. Jena, K.C. Das, Comparative evaluation of thermochemical liquefaction and pyrolysis for bio-oil production from microalgae, *Energy Fuel* 25 (2011) 5472–5482.
- [17] (a) T.M. Brown, P. Duan, P.E. Savage, Hydrothermal liquefaction and gasification of *Nannochloropsis* sp. *Energy Fuel* 24 (2010) 3639–3646; (b) P. Duan, P.E. Savage, Hydrothermal liquefaction of a microalga with heterogeneous catalysts, *Ind. Eng. Chem. Res.* 50 (2011) 52–61; (c) P.J. Valdez, M.C. Nelson, H.Y. Wang, X.N. Lin, P.E. Savage, Hydrothermal liquefaction of *Nannochloropsis* sp.: systematic study of process variables and analysis of the product, *Biomass Bioenergy* 46 (2012) 317–331.
- [18] C. Jazrawi, P. Biller, A.B. Ross, A. Montoya, T. Maschmeyer, B.S. Haynes, Pilot plant testing of continuous hydrothermal liquefaction of microalgae, *Algal Res.* 2 (2013) 268–277.
- [19] J.A. Olivares, *Biorefining magazine*, [http://biorefiningmagazine.com/articles/5460/overview-of-naabbundefineds-algal-biofuels-consortiumApril 19 2011](http://biorefiningmagazine.com/articles/5460/overview-of-naabbundefineds-algal-biofuels-consortiumApril%2019%202011) (last accessed May 2, 2013).
- [20] D.C. Elliott, G.G. Neuenschwander, T.R. Hart, L.J. Rotness, A.H. Zacher, D.M. Santosa, C. Valkenburg, S.B. Jones, S.A. Tjokro-Rahardjo, Catalytic hydrothermal gasification of lignin-rich biorefinery residues and algae, PNNL-18944, Pacific Northwest National Laboratory, Richland, Washington, 2009.
- [21] D.C. Elliott, T.R. Hart, Catalyst and method for aqueous phase reactions. U.S. Patent #5,977,013, issued November 2, 1999.
- [22] D.C. Elliott, T.R. Hart, G.G. Neuenschwander, L.J. Rotness, M.V. Olarte, A.H. Zacher, Y. Solantausta, Catalytic hydroprocessing of fast pyrolysis bio-oil from pine sawdust, *Energy Fuel* 26 (2012) 3891–3896.
- [23] P. Duan, P.E. Savage, Upgrading of crude algal bio-oil in supercritical water, *Bioresour. Technol.* 102 (2011) 1899–1906.
- [24] Z. Li, P.E. Savage, Feedstocks for fuels and chemicals from algae: treatment of crude bio-oil over HZSM-5, *Algal Res.* 2 (2013) 154–163.
- [25] D.C. Elliott, T.R. Hart, G.G. Neuenschwander, Chemical processing in high-pressure aqueous environments. 8. Improved catalysts for hydrothermal gasification, *Ind. Eng. Chem. Res.* 45 (2006) 3776–3781.
- [26] Y. Zhu, K.O. Albrecht, D.C. Elliott, R.T. Hallen, S.B. Jones, Development of hydrothermal liquefaction and upgrading technologies for lipid-extracted algae conversion to liquid fuels, *Algal Res.* 2 (2013) 455–464.
- [27] E.D. Frank, A. Elgowainy, J. Han, Z. Wang, Life cycle comparison of hydrothermal liquefaction and lipid extraction pathways to renewable diesel from algae, *Mitig. Adapt. Strateg. Glob. Change* 18 (2013) 137–158, <http://dx.doi.org/10.1007/s11027-012-9395-1>.