# Hydrothermal Processing of Macroalgal Feedstocks in Continuous-Flow Reactors

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ABSTRACT: Wet macroalgal slurries have been converted into a biocrude by hydrothermal liquefaction (HTL) in a bench-scale continuous-flow reactor system. Carbon conversion to a gravity-separable oil product of 58.8% was accomplished at relatively low temperature (350 °C) in a pressurized (subcritical liquid water) environment (20 MPa) when using feedstock slurries with a 21.7% concentration of dry solids. 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 mineral components were removed by processing steps so that they did not cause processing difficulties. In addition, catalytic hydrothermal gasification (CHG) was effectively applied for HTL byproduct water cleanup and fuel gas production from water-soluble organics. Conversion of 99.2% of the carbon left in the aqueous phase was demonstrated. As a result, high conversion of macroalgae to liquid and gas fuel products was found with low levels of residual organic contamination in byproduct water. Both process steps were accomplished in continuous-flow reactor systems such that design data for process scale-up was generated.

KEYWORDS: Hydrothermal, Liquefaction, Catalyst, Gasification, Aqueous phase, Macroalgae
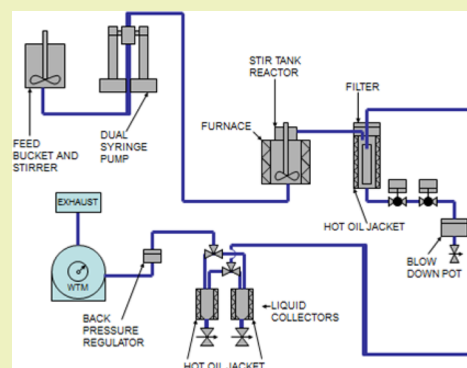
INTRODUCTION

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 macroalgal biomass, it contains substantial nitrogen as well. The processing option is particularly applicable to wet biomass feedstocks, such as marine-grown macroalgae.

Macroalgae, commonly referred to as seaweed, has commercial uses as human food, animal feed, fertilizers and soil conditioners, and feedstock for hydrocolloid extraction.[1] The total commercial harvest in 2010 was 19.9 million wet tonnes, with aquaculture accounting for 96% of the harvest.[2] Interest in macroalgae as a feedstock for fuel production stems from efforts in the 1970s and 1980s to investigate both offshore macroalgae production and its conversion to methane.[3] The feasibility of producing methane by anaerobic digestion from macroalgae was considered competitive with that from terrestrial biomass.[4] More recently, production of macroalgae at the scale needed for producing biofuels is under active investigation again, and considerable progress is being made in conversion of macroalgae to various fuel types that in addition to methane include ethanol[5] and butanol[6] by fermentation and hydrothermal liquefaction to bio-oils.[7,8]

HTL requires processing in a high-pressure system (20 MPa) that maintains liquid water, even at the high temperatures (350 °C) used in the conversion. The reactor system used at Pacific Northwest National Laboratory (PNNL) also provides a means to effectively separate the product bio-oil from the byproduct water and recover the mineral byproducts and gas byproducts

for analysis. Slurries are processed through 1 L continuous-flow stirred tank reactors, and the products are recovered.

Elliott recently reviewed the early work in hydrothermal processing of wet biomass for both liquid and gas fuel production.[9] Recent reports in the literature that have described HTL and its application to microalgae have been primarily related to batch reactor tests as reported by Chow et al.[10] except that we have very recently reported continuous-flow HTL.[11] In that paper, we also reported continuous-flow catalytic processing by hydrothermal gasification of the aqueous byproduct from microalgae HTL. Here, we report the preliminary results of continuous-flow reactor studies of hydrothermal liquefaction with wet macroalgae feedstock. Subsequent 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 that more direct disposal will be possible.

BACKGROUND

There have been relatively limited studies of the use of hydrothermal processing (high-pressure, high-temperature, liquid water).[9] Although process development of direct liquefaction of biomass for fuels production can be traced to the work related to the Albany, Oregon, Biomass Liquefaction Experimental Facility, significant development has languished in the United States for
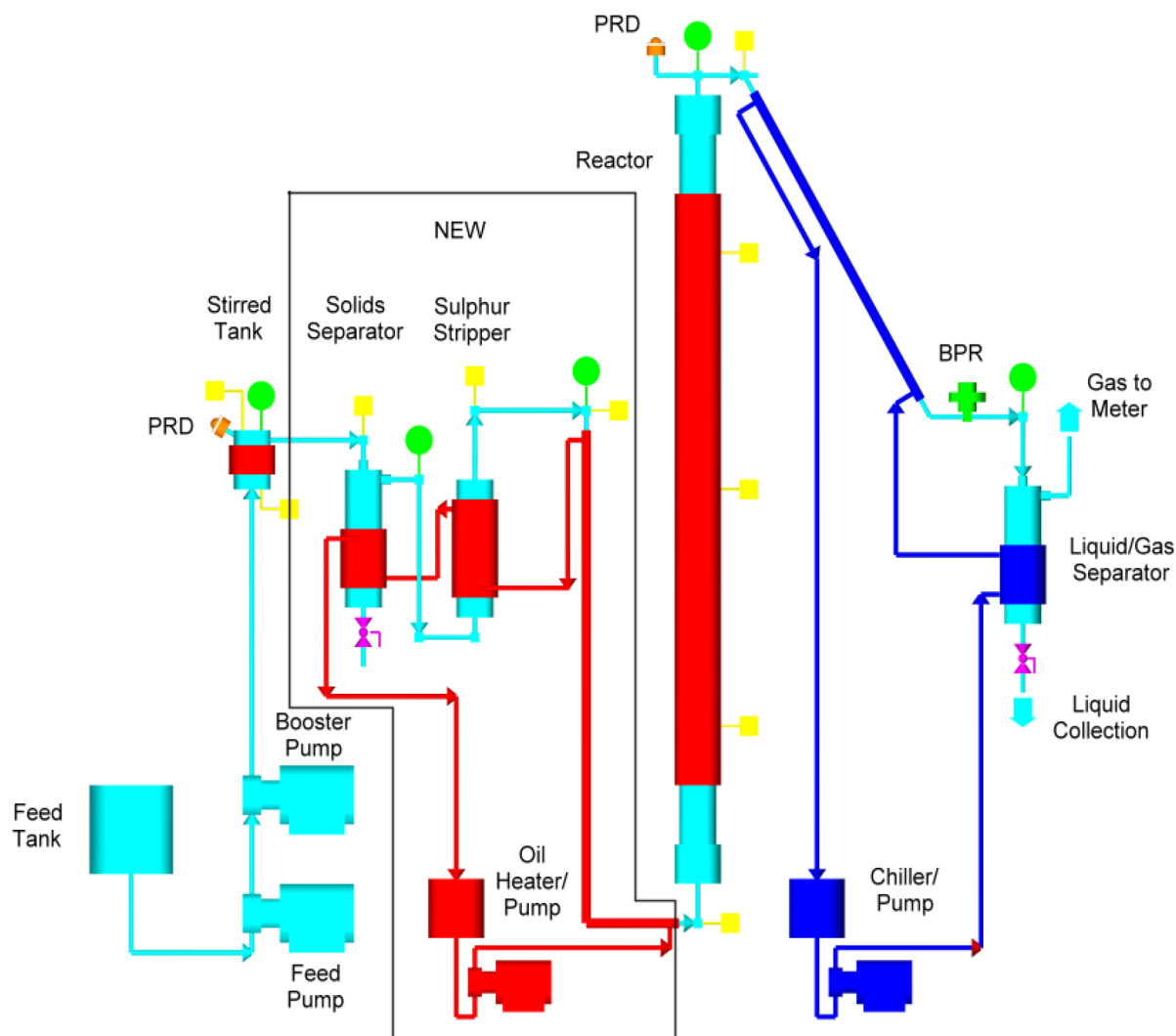
Figure 1. Schematic of the bench-scale continuous-flow reactor system (original CHG configuration). PRD = pressure relief device, BPR = back pressure regulator, yellow squares = thermocouples, and green circles = pressure sensors.

the last three decades due to the difficulties experienced in the high-pressure processing of fibrous lignocellulosic feedstocks. This article provides new results of hydrothermal liquefaction (HTL) using as the feedstock macroalgae, whose structure is more amenable to forming pumpable slurries.

Recently, microalgae biomass has received attention as a feedstock for HTL, but macroalgae has been mostly overlooked, probably because of the higher lipid content in microalgae and the perception of potential for higher bio-oil yield. HTL is an appropriate conversion process to utilize algae without drying, thus minimizing parasitic energy requirements. HTL can be used in this application for biocrude production utilizing all 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.[12]

Elliott et al.[7] published the first report of HTL of macroalgae (*Macrocystis sp.*) using a batch reactor fed with kelp dry mass at 10 wt % in water. After 4 h at 350 °C, they reported an oil yield of 19.2 wt % based on solvent separation of oil product. There have been a few recent reports on HTL of wet macroalgal biomass. Anastassakis and Ross,[8] Zhou et al.,[13] and Li et al.[14] have tested HTL of marine macroalgae. In their work, similar

processing conditions have been evaluated with different algae, *Enteromorpha prolifera*, *Laminaria saccharina*, and *Sargassum patens* C. Agardh. These reports taken together develop a consensus that macroalgae can be processed by HTL into a complex mixture oxygenated hydrocarbons that is liquid at or near room temperature at a high mass yield. A complementary study shows that noncatalytic hydrothermal gasification of four other species of macroalgae in supercritical water at 500 °C was also effective in producing hydrogen, carbon dioxide, and methane gas in yields of 75−95%.[15]

Thus far, the reports of all these groups have been limited to batch reactor testing, so the results are of limited value for developing the kinetics of an industrially useful continuous-flow process. In addition, the use of small batch reactors led the investigators in most cases 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. Some researchers[15] have proposed that the extensive amount of organic remaining in the water was a potential source for value-added products, such as by fermentation of sugars, while others proposed direct recovery of the more prominent light oxygenates, e.g., acetic acid and
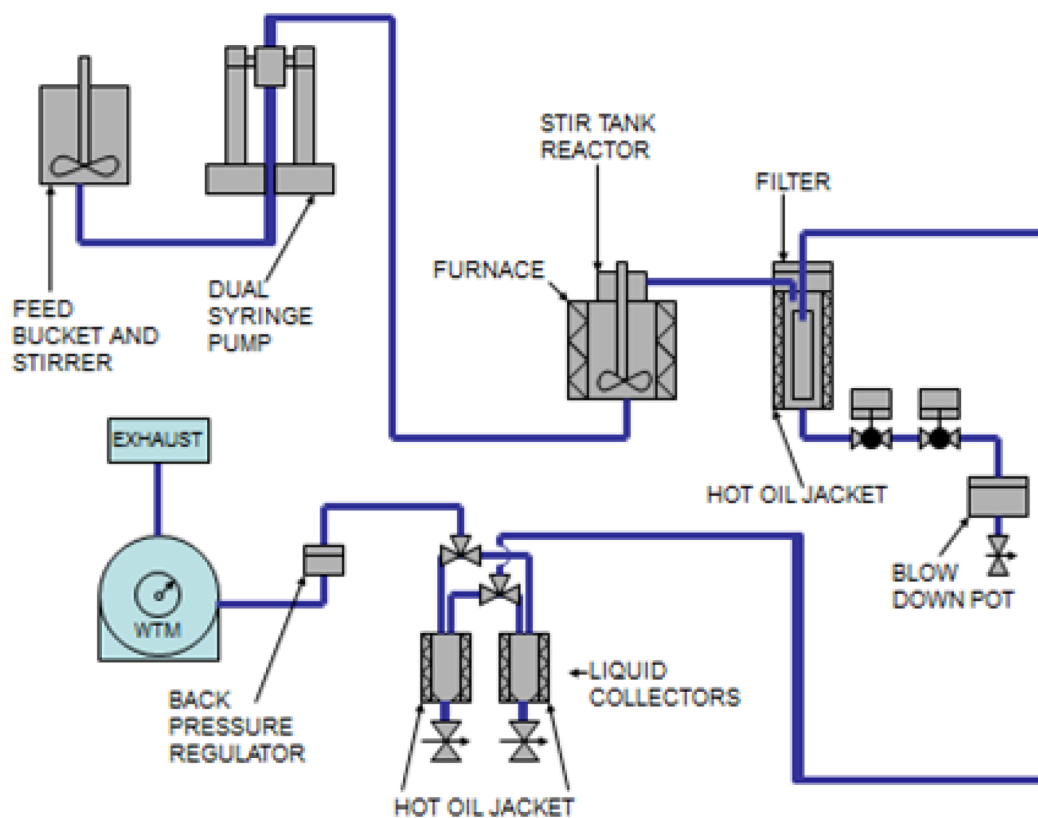
Figure 2. Schematic of the bench-scale continuous-flow reactor system (revised HTL configuration).

glycerol, as chemical products. In this study, we demonstrate the use of catalytic hydrothermal gasification (CHG) as an effective straightforward means to recover the fuel value of the dissolved organics as a medium heating value gas composed primarily of methane and carbon dioxide as has been demonstrated earlier for the aqueous byproduct from microalgae HTL.[11]

■ EXPERIMENTAL SECTION

The kelp, *Saccharina spp.*, was collected from natural beds off Rocky Point, WA, by scuba divers. Blades were separated from holdfasts and stipes, frozen at −20 °C, and transported on dry ice prior to conversion experiments.

The equipment and procedures described below were used for testing the hydrothermal liquefaction of wet macroalgae slurries as well as the catalytic hydrothermal gasification of the organics left in the byproduct water stream. The work at PNNL reported here has used bench-scale continuous-flow reactor systems for both HTL and CHG.

Hydrothermal Processing. A continuous-flow reactor system was originally designed for obtaining engineering data for the CHG process and has been described in the literature previously.[11] The system essentially consists of the high-pressure pump feeding system including the feed tank, feed pump, and booster pump, the 1 L stirred tank preheater, and the 1 L tubular catalytic reactor. The mineral separation was done via two 1 L high-pressure vessels, the solids separator, and the sulfur stripper. Following passage through a chiller and pressure letdown by a back-pressure regulator (BPR), separation was made of gases and liquid products. 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 Figure 1. The modifications implemented for handling minerals (via a solids separator) and sulfur (via a stripper) in the macroalgae feedstocks are indicated in the outline labeled "NEW." These two components are maintained at near reaction temperature by a circulating oil heater.

The modified system as shown in Figure 2 was used for HTL. In that case, the sulfur scrubber and tubular reactor were bypassed, and a modified liquid product collection system was used in its place.

The macroalgae feedstock pretreatment and preparation method was designed to ensure a homogeneous feed for the reactor with a purée-like consistency. The feedstocks typically required a wet milling step in a Union Process attrition mill. The slurry feedstocks were prepared by grinding macroalgae fronds in DI water in the stirred ball mill until it reached the proper consistency to pass through a 60 mesh screen. For the CHG tests with the HTL aqueous byproduct, no feedstock preparation was required.

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

The CHG reactor system was used for HTL except with the omission of the catalytic reactor and some modification to allow biocrude liquid product separation from the aqueous byproduct stream and the collection of both. In the HTL tests, the stirred tank preheater was essentially the reactor. It was a 1 L 316 SS vessel equipped with internal stirring propellers.

Following liquefaction, it was possible to separate mineral matter from the process 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. We placed a solids separator vessel, equipped with a filter in the process line following the reactor, to capture and remove the solids following heat-up to reaction temperature. The design of the separator was a simple dip leg vessel wherein the solids fell to the bottom of a vessel, and the liquids passed overhead through a filter. The solids could be removed by batch from the bottom of the vessel via the blow down pot as they built up over time. We found that by using this in-line system a solids-free bio-oil product would be more readily separated from the water phase.

Table 1. HTL Feedstocks Analyses[a]

	#1	#2	#3	#4	#5[b]	#6[b]
carbon, wt % dry	31.1	33.8	34.0	21.3	33.7	32.5
hydrogen, wt % dry	4.4	4.4	4.8	4.8	4.4	4.4
oxygen, wt % dry	34.1	34.8	36.7	36.7	33.2	32.2
nitrogen, wt % dry	2.2	2.6	1.5	2.1	2.0	2.6
sulfur, wt % dry	0.8	1.0	0.6	0.9	0.7	1.5
ash, wt %	23.6	22.3	11.5	41.1	32.4	27.0
density, g/mL @ 40 °C	1.01	0.90	0.87	0.91	nd[c]	1.09
pH	nd	nd	nd	nd	5.12	nd
chemical oxygen demand, ppm	41,867	85,600	105,290	93,500	160,000	231,942

[a]C, H, N, and O by ASTM D5373; S by ASTM D4239. [b]Pretreated at 175 °C. [c]nd = not determined.

Table 2. Process Data for Macroalgae Hydrothermal Liquefaction

	#1	#2	#3	#4	#5[a]	#6[a]
temperature, °C	350	358	354	350	354	364
pressure, MPa	20.1	20.7	20.2	20.2	20.2	20.6
LHSV, L/L/h	1.17	1.22	1.23	1.26	1.21	1.51
dry solids, wt %	5.3	13.0	5.0	10.0	16.1	21.7
carbon gasification, %	7.6	6.9	14.8	7.8	1.4	3.2
carbon to aqueous, %	73.9	49.1	60.9	54.1	53.1	34.9
carbon loss in solid, %	1.4	2.8	0.4	0.1	0.2	4.3
carbon in oil, %	17.1	41.3	24.0	38.1	45.3	57.6
carbon closure, %	80	44	98	65	92	85
mass closure, %	101	104	103	111	112	101
energy yield, %	20.3	53.4	28.8	44.4	51.6	52.0

[a]Thermally pretreated to 175 °C to dewater the biomass.

In the CHG tests, the preheated feed from the stirred tank passed through the solids separator as well as a sulfur stripper before entering the 1 L tubular reactor with the fixed catalyst bed where the gasification took place in an up-flow configuration. In this configuration, the "new" in-line cleanup system served to protect the catalyst bed in the tubular reactor from mineral deposits and sulfur poisoning. The catalyst used was ruthenium metal, 7.8% on a partially graphitized carbon extrudate. The sulfur scrubber was filled with a pelletized form of Raney nickel.

In HTL mode, after exiting the solids separator, the products were conducted to a dual liquids collecting system wherein the condensed liquids were collected at high pressure. Periodically, the collection vessel was isolated by valving, 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 vented overhead through a back-pressure regulator to the process vent where it was metered and sampled for offline gas chromatography analysis.

The product liquids were drained from the collectors into 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. Weight percent C, H, N, O, and S was analyzed by ASTM methods D5291, D5373, and D4239 and trace element analysis by ICP-OES as described previously.[11] The total acid number (TAN) was analyzed by D3339 and the moisture by E1064. 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.[11]

Gas samples could be withdrawn manually from the vent line and analyzed every 30−60 min. In the HTL mode, the gaseous stream was mainly composed of CO_2 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.[11]

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

RESULTS AND DISCUSSION

The testing discussed here produced initial results for continuous-flow processing of wet macroalgae feedstocks in the bench-scale reactor system. The HTL process was operated at nominally 20 MPa and 350 °C with a liquid hourly space velocity ranging from 1.2 to 1.5 L of slurry per liter of reactor volume per hour using macroalgae slurries at 5−22 wt % dry solids. The macroalgae tested was *Saccharina spp*. The feedstock analyses are provided in Table 1.

The six feedstocks vary in composition because they represent six different harvest times and harvesting conditions, as might represent the variability of the feedstock in a real world application. The composition of this macroalgae feedstock is reported[16] to include only a small amount of lipids (2%), compared to much higher levels in some microalgae, with a significant protein component (12%) and carbohydrate structures including cellulose (6%), other sugar alcohol structures, such as mannitol and laminarin (26%), and sugar acid structures like alginic acid and fucoidins (31%); however, it contains essentially no lignin.

A total of six HTL tests were performed; two of the aqueous byproduct streams were gasified. The process conditions tested in HTL are given in Table 2. The liquid products (bio-oil and aqueous phase) and solid products (from the mineral separator) were directly recovered, and their masses were determined. The product gas volume was measured, and the composition was determined by GC. The carbon distribution in the product slate is also given in Table 2. The last two tests included a pretreatment step that involved batch heating of the

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kelp to breakdown the cellular structure and volatilize a portion of the intracellular moisture. With this step, a small increase in the biomass concentration was achieved.

The most obvious trend in the data is the increase in water-separable biocrude production with the increase in biomass dry solids concentration in the feedstock slurry. The inverse of carbon remaining in the aqueous stream is a corollary result. Carbon remaining as residual solids is low as is the gasification of carbon. Overall, carbon recovery was variable in the several tests due to the difficulty of product hangup in the reactor system as a function of the short experimental period. The carbon closure is based on the direct carbon analysis of the feedstock and the solid and liquid products and the calculated carbon content of the gas based on the composition determined by GC analysis.

The experiments varied from 1/2 to 6 h following the startup period. The experiments were performed on separate days of operation, and their lengths were limited by the small amount of feedstock available. The most abundant trace metals were K, Na, Ca, Mg, and P, found at 93000, 29000, 5400, 6400, 6700 mg/kg, respectively, in feed #6. The ash in these macroalgae resulted in little mineral precipitation, and no mineral blowdown was required during the short process tests nor were significant amounts of precipitate recovered from the separator vessel following the tests. The tests were routinely terminated when the feedstock supply was exhausted.

The bio-oil was directly recovered by gravity separation from the aqueous byproduct after draining from the liquid product collectors, in contrast to earlier batch work by others, which invariably required a solvent wash for bio-oil recovery from the reactor. The process products for hydrothermal liquefaction are given in Table 3. Contrary to tests with microalgae,[11] the aqueous product is where most of the carbon is recovered when a low concentration feedstock slurry is used, as shown by the product yields in Table 2. However, because there is such a large fraction of feed slurry that is water, the carbon level found in the aqueous phase byproduct is actually quite small. It seems to be saturated with water-soluble bio-oil components at a level of 1–2% carbon. The HTL biocrude product is a mostly deoxygenated viscous oil, and its composition reflects the biostructures mentioned above in the macroalgae. Compared to HTL oil from lignocellulosics produced in the same reactor system,[12] it is similar in density, contains substantial dissolved water, and has a high acid content (TAN). On the other hand, it has higher nitrogen and sulfur contents. It appears more similar to the lignocellulosic HTL biocrude than that produced from microalgae.[11] Although the aqueous phase from HTL accounts for a large fraction of the C in the feedstock, it contains only a low level of C.

A simple process energy yield calculation can be made based on the higher heating value of the bio-oil product compared to the higher heating value of the feedstock. Using the formula of Channiwala and Parikh,[17] the feed and product energy contents were calculated. The energy yields were calculated as a percentage of the energy in the feed recovered as energy in the bio-oil, and those results are provided in Table 2. The efficiency falls in the range of 52–53% for experiments performed with feedstock concentration of 13–22% but is only 20–44% for feedstock concentrations from 5–10%.

Contrary to tests with microalgae,[11] N was not detectable in the aqueous phase in four of the six tests and amounts to only a small fraction in those tests where it was detected.

The larger N release into the aqueous phase in test #6 may have resulted from the slightly higher processing temperature. The aqueous has a nearly neutral pH due to the dissolved alkali available to neutralize the residual organic acids, represented by the substantial COD. The gas product is mostly CO_2 with some H_2 found in half the cases; the levels of CO and CH_4 were below the level of detection. In these process tests, the small amount of gas product was highly diluted by N_2 pressurization gas in the liquid collectors, so that the gas analyses were inconsistent.

Chloride is another significant factor as the macroalgae were grown in a marine environment. No evidence of corrosion was found in these limited tests.

GC-MS analysis of the HTL oil product showed an interesting collection of components suggesting the production of the oil from the carbohydrates and proteins in the macroalgae. The components (cyclic ketones and phenolics) are more similar to those seen from HTL of lignocellulosic biomass than from microalgae in that they do not contain the long-chain hydrocarbons derived from lipids (fatty acids and amides). The chromatograph, shown in Figure 3 (which only represents the volatile portion of the product), showed a complex mixture of light compounds through phenolic compounds. The "alkyl" descriptor includes methyl, ethyl, dimethyl, trimethyl, and tetramethyl. These were essentially all heterocyclic compounds containing N and/or O. These results compare favorably with Schumacher et al., who also reported these products in batch tests.[15] Our results were only semiquantitatively determined by total ion count.

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. Attempts to determine the elemental balance of these components using less than optimal analytical methods have given inconsistent results thus far. Table 4 gives data for the #6 HTL test, listing the amounts of material and concentrations to determine actual amounts of elements. The caption, "portion of feed recovered", indicates the portion of the respective element present in the feed that was subsequently recovered in the several product fractions. "Selectivity" is the normalized distribution of the elements in the products.

The data suggests that the P accounting is short of the total in the feed. The only recovered P was in the precipitated solids. The small recovery of solids suggest 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 because that is the method for sample preparation for the analysis.

The data for N provided an over-recovery of 126%. In this case, nearly half of the N would be available for direct recycle as dissolved ammonium in the aqueous byproduct. 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 balance of the N appeared split between the gas product and the biocrude product. 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 N_2) provided a mechanism for 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 N that reports to the oil

Table 3. HTL Products[a]

	#1	#2	#3	#4	#5	#6
Bio-oil						
yield, wt % DAF[b]	8.7	23.6	11.5	16.9	27.1	27.7
carbon, wt% dry	79.2	78.8	80.9	81.0	79.4	69.0
hydrogen, wt% dry	8.5	9.4	9.1	8.6	8.0	7.5
oxygen, wt% dry	7.5	7.2	6.5	5.6	8.3	1.8
nitrogen, wt% dry	4.1	4.1	3.3	4.1	4.1	4.4
sulfur, wt% dry	0.6	0.5	0.2	0.7	0.3	0.6
moisture, wt%	7.3	6.4	5.9	23.3	9.2	13.4
density, g/mL@40 °C	1.05	1.04	1.03	1.03	1.03	1.02
viscosity, cSt @40 °C	5698	1436	3652	5958	1708	1579
TAN, mg KOH/g	nd[c]	nd	nd	nd	36	38
Aqueous						
carbon, wt%	1.0	0.9	1.0	0.7	2.5	2.4
nitrogen, wt%	<0.05	<0.05	<0.05	<0.05	0.1	0.3
chloride, ppm	49	nd	76	85	2533	nd
sulfate, ppm	6.6	nd	5.1	6.7	186	nd
pH	7.2	6.9	7.3	7.2	7.2	7.2
COD, mg/kg	29,300	41,467	64,900	24,740	65,325	76,783
Gas						
CO_2, vol%	73	99	86	99	70	85
H_2, vol %	27	0	14	0	30	0
CO, vol %	0	0	0	0	0	1
CH_4, vol %	0	0	0	0	0	4
ethane, vol %	0	0	0	0	0	2
NH_3, vol % (tentative)	nd	nd	nd	nd	nd	8

[a]C, H, and N by ASTM D5373/D5291; O by ASTM D5373 modified; S by ASTM D4239. [b]DAF = dry, ash-free basis. [c]nd = not determined.
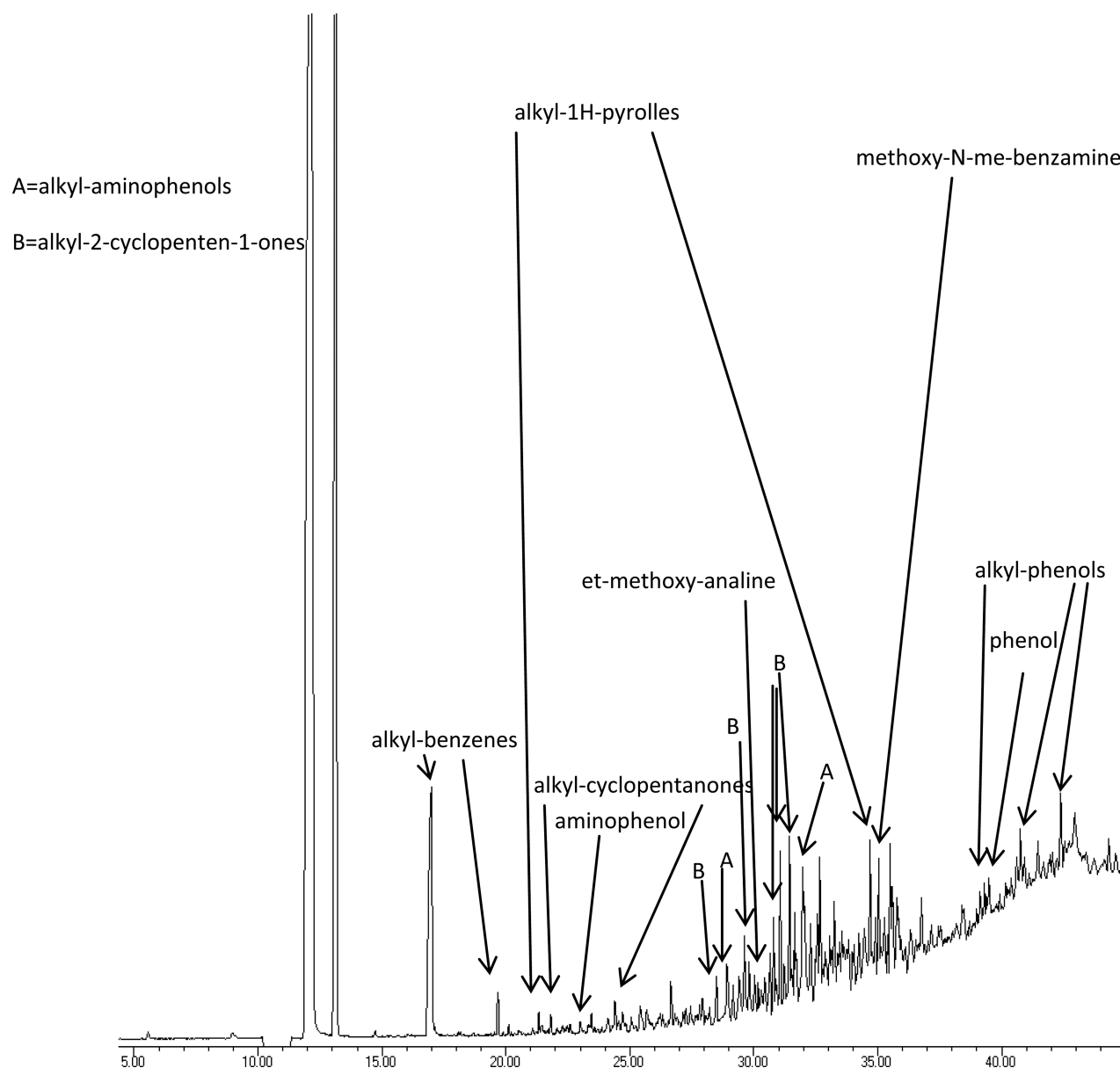
Figure 3. Total ion chromatograph of macroalgae HTL biocrude in methanol solvent.

Table 4. Nutrient Balance for #6 HTL

phosphorus balance				
component	concentration (ppm)	amount (g/h)	portion of feed recovered (%)	selectivity, normalized (%)
feed, 356.2 dry g/h	6710	2.39		
solid, 12.64 g/h	56,740	0.72	30	100
aqueous, 1461 g/h	0	0.0	0	0
oil, 84 g/h	0	0.0	0	0
nitrogen balance				
component	concentration (wt %)	amount (g/h)	portion of feed recovered (%)	selectivity, normalized (%)
feed, 356.2 dry g/h	2.60	9.26		
solid, 12.64 g/h	2.35	0.30	3	3
aqueous, 1461 g/h	0.31	4.53	49	39
oil, 84 g/h	4.26	3.58	39	31
gas,18.6 L/h	25 vol%	3.29	36	28

product in this case is significant. There was little residual sulfate in the HTL aqueous byproduct that was used as CHG feedstock. No effort was made to precipitate this sulfate before it could enter the catalyst bed and poison the catalyst. Calcium hydroxide has been added in stoichiometric excess for this effect in other applications.[11]

Table 5. Trace Element Balance for HTL Feeds and Separated Solids, Dry Basis

component	Na ppm	K ppm	Ca ppm	S ppm	P ppm	Mg ppm	Si ppm	Fe ppm
#2 feed	22,400	64,000	6400	10,700	4800	5000	460	4400
#2 blowdown	15,600	7400	134,000	73,200	61,500	26,900	180	28,500
#6 feed	29,400	92,900	5400	15,100	6710	6400	630	220
#6 blowdown	17,600	41,700	54,000	17,800	56,700	48,100	1900	2600

Tracking of other trace elements in the feedstock was of interest. The analysis by ICP-OES provided the data presented in Table 5. We found that alkali metals, Na and K, were present in the feedstock but were significantly reduced in the separated solids stream, suggesting that they remained dissolved in the aqueous. The Ca, Mg, and P were found to be highly concentrated in the separated solids, as reported above in the P balance calculations. S and Fe were also concentrated, while analysis of Si gave conflicting results.

HTL Aqueous Recycle. The recycle of the HTL aqueous byproduct was undertaken in a bench-scale batch reactor system to determine if an additional biocrude product could be generated from the organic content in the water. The processing information is given in Table 6 for a process test using

Table 6. Process Parameters for Batch Hydrothermal Liquefaction of Aqueous Byproduct

	#1
temperature, °C	350
pressure, MPa	autogenic
time at temperature, h	4
feedstock COD, g/kg	23
product COD, g/kg	23

as feedstock the aqueous byproduct from HTL test #1 described above. The processing conditions were essentially the same as for liquefaction to allow additional time at temperature and pressure to facilitate appropriate condensation reactions for water-insoluble oil formation from the water-soluble organics. Such reactions have been suggested in the literature as a result of Aldol condensation mechanisms among others.[18]

The batch recycle HTL of the aqueous byproduct resulted in effectively no reaction as shown by the results in Table 6. The COD of the water was unchanged following 4 h at 350 °C, and no recoverable oil was produced. There as a slight char formation noted on the wall of the reactor but no recoverable mass.

HTL Aqueous Gasification. Because there was a large fraction of the macroalgae remaining dissolved in the aqueous byproduct, energy recovery from that stream was suggested as a possible use. The catalytic hydrothermal gasification (CHG) of the HTL aqueous byproduct was undertaken in a continuous-flow bench-scale reactor system to verify the recovery of the energy content of the organic content in the water by conversion to a medium heating value fuel gas. This step could be a process water cleanup addendum to liquefaction as well as an alternative energy recovery method. The processing information is given in Table 7 for a process test using as feedstock the byproduct from HTL tests #1 and #2 described above. The processing conditions are essentially the same as for liquefaction thus facilitating the integration of the two processes assuming a high-temperature, high-pressure, liquid phase separator to recover the biocrude product separate from the aqueous by-

Table 7. Process Parameters for Hydrothermal Gasification of HTL Aqueous Byproduct

	#1	#2
temperature, °C	348	345
pressure, MPa	20.0	20.0
LHSV, L/L/h	1.89	1.85
feedstock COD, g/kg	23	31

product. The catalyst composition used was 7.8 wt % ruthenium metal on a partially graphitized carbon extrudate. The activity and stability of this catalyst has been demonstrated previously.[19]

The CHG of the HTL aqueous byproduct resulted in nearly complete gasification of the remaining organic components as shown by the results in Table 8. COD of the water was reduced

Table 8. Product Compositions from CHG of HTL Aqueous Byproduct

	#1	#2
Aqueous		
pH	6.9	7.1
COD, mg/kg	30	310
Gas		
carbon dioxide, vol %	28	41
hydrogen, vol %	0.4	0.8
carbon monoxide, vol %	0	0
methane, vol %	69	57
higher hydrocarbons, vol %	0	0

by >99%. The typical high methane and carbon dioxide gas was produced with little hydrogen or higher hydrocarbons. The results presented in Table 8 are for 8.5 h of operation.

Starting at 23,400 ppm COD in the aqueous byproduct and using a 1.89 LHSV, a 99.7% conversion of the COD was accomplished. The gas product was 70% methane and 29% carbon dioxide with 0.9% hydrogen residual. Later in the test, a slightly more concentrated product was processed with similar results. Starting at 31,300 ppm COD in the aqueous byproduct and using a 1.85 LHSV, a 99.2% conversion of the COD was accomplished. The gas product was 58% CH_4 and 42% CO_2 with 0.4% H_2 residual.

This was only a short test of a little over 8 h, but it showed that the preheater stayed clean with only a slight coating of coke noted. Analysis of this material suggested that the grinding media metals were a major factor in the coke formation. The mineral precipitate was minimal (1–4% of the blowdown after the test), and its constituents were the expected components consisting of the grinding media metals along with feedstock-derived Ca, P, S, and Mg, suggesting insoluble alkaline earth phosphates and sulfates, while the K and Na (the major mineral components in the macroalgae) were more likely to remain dissolved. The Cl concentration was high enough to require dilution of the samples to remove a chloride interference in the COD determination.

CONCLUSIONS

In this work, the kelp, *Saccharina spp.*, has been converted by hydrothermal liquefaction into a bio-oil with an oxygen content of <8% calculated to a dry basis. The biocrude product was recoverable by gravity separation, but the oil yield is low. Also, much or most of the organic (depending on the feed slurry concentration) remains dissolved in the water byproduct. There is little gas byproduct. The macroalgae feedstocks were processed at slurry concentrations of up to 22 wt % dry solids. The yield of oil increased with increasing concentration of the slurry feedstock, approaching 60% on a carbon basis with feed concentration at about 22 wt % dry solids, and this relationship is clearly the direction for future research. Analysis of the biocrude content suggested that it consisted of heterocyclics derived from the biomass components. 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. The mineral matter was, for the most part, recovered in the aqueous byproduct, and only to a limited degree did it precipitate at hydrothermal conditions.

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 (little of which was done in this short study); and demonstrating the effectiveness of separation techniques to remove precipitated nutrients (primarily phosphate, but also sulfate) before catalyst poisoning. Recycling of nutrients from the recovered byproducts (P in solids and N, K, and C in aqueous) is a potential area for process cost savings and improved sustainability. Scale-up of the processing equipment may identify potential issues, which may need to be resolved, e.g., high-pressure slurry pumping and heat exchange, mineral separation, and oil/water separation.

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Notes
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REFERENCES

(1) McHugh, D. J. *A Guide to the Seaweed Industry*; Food and Agricultural Organization (FAO): Rome, **2003**.

(2) *Fisheries and Aquaculture Statistics 2010*; Food and Agricultural Organization (FAO): Rome, 2012.

(3) Bird, K. T.; Benson, J. *Seaweed Cultivation for Renewable Resources*; Elsevier Science Ltd.: Amsterdam, 1987.

(4) Chynoweth, D. P.; Owens, J. M.; Legrand, R. Renewable methane from anaerobic digestion of biomass. *Renewable Energy* **2001**, *22* (1−3), 1−8.

(5) ((a)) Horn, S. J.; Aasen, I. M.; Ostgaard, K. Ethanol production from seaweed extract. *J. Ind. Microbiol. Biotechnol.* **2000**, *25* (5), 249−254. ((b)) Wargacki, A. J.; Leonard, E.; Win, M. N.; Regitsky, D. D.; Santos, C. N. S.; Kim, P. B.; Cooper, S. R.; Raisner, R. M.; Herman, A.; Sivitz, A. B.; Lakshmanaswamy, A.; Kashiyama, Y.; Baker, D.; Yoshikuni, Y. An engineered microbial platform for direct biofuel production from brown macroalgae. *Science* **2012**, *335* (6066), 308−313.

(6) Huesemann, M. H.; Kuo, L.-J.; Urquhart, J.; Gill, G. A.; Roesijadi, G. Acetone-butanol fermentation of marine macroalgae. *Bioresour. Technol.* **2012**, *108*, 305−309.

(7) Elliott, D. C.; Butner, R. S.; Sealock, L. J., Jr. Product Analysis from Direct Liquefaction of Several High-Moisture Biomass Feedstocks. In *Pyrolysis Oils from Biomass: Producing, Analyzing, and Upgrading*; Soltes, E. J., Milne, T. A., Eds.; ACS Symposium Series 376; American Chemical Society: Washington, DC, 1988; pp 179−188.

(8) Anastasakis, K.; Ross, A. B. Hydrothermal liquefaction of the brown macro-algae *Laminaria saccharina*: Effect of reaction conditions on product distribution and composition. *Bioresour. Technol.* **2011**, *102*, 4876−4883.

(9) Elliott, D. C. Hydrothermal Processing. In *Thermochemical Processing of Biomass: Conversion into Fuels, Chemicals and Power*; Brown, R.C., Ed.; John Wiley & Sons, Ltd.: Chichester, U.K.; 2011; pp 200−231.

(10) Chow, M. C.; Jackson, W. R.; Chaffee, A. L.; Marshall, M. Thermal treatment of algae for production of biofuel. *Energy Fuels* **2013**, *27*, 1926−1950.

(11) Elliott, D. C.; Hart, T. R.; Schmidt, A. J.; Neuenschwander, G. G.; Rotness, L. J.; Olarte, M. V.; Zacher, A. H.; Albrecht, K. O.; Hallen, R. T.; Holladay, J. E. *Algal Res.* **2013**, accepted for publication.

(12) Toor, S. S.; Rosendahl, L.; Rudolf, A. Hydrothermal liquefaction of biomass: A review of subcritical water technologies. *Energy* **2011**, *36*, 2328−2342.

(13) Zhou, D.; Zhang, L.; Zhang, S.; Fu, H.; Chen, J. Hydrothermal liquefaction of macroalgae *Enteromorpha prolifera* to bio-oil. *Energy Fuels* **2010**, *24*, 4054−4061.

(14) Li, D.; Chen, L.; Xu, D.; Zhang, X.; Ye, N.; Chen, F.; Chen, S. Preparation and characteristics of bio-oil from the marine brown alga *Sargassum patens* C. Agardh. *Bioresour. Technol.* **2012**, *104*, 737−742.

(15) Schumacher, M.; Yanik, J.; Sinag, A.; Kruse, A. Hydrothermal conversion of seaweeds in a batch autoclave. *J. Supercrit. Fluids* **2011**, *58*, 131−135.

(16) Reith, J. H.; Deurwaarder, E. P.; Hemmes, K.; Curvers, A. P. W. M.; Kamermans, P.; Brandenburg, W.; Zeeman, G. *Grootschalige teelt can zeewieren in combinatie met offshore windparken in de Nordzee*; Energy Research Center of the Netherlands: Petten, The Netherlands, **2005**.

(17) Channiwala, S. A.; Parikh, P. P. A unified correlation for estimating HHV of solid, liquid and gaseous fuels. *Fuel* **2002**, *81*, 1051−1063.

(18) Nelson, D. A.; Hallen, R. T.; Theander, O. Formation of aromatic compounds from carbohydrates. In *Pyrolysis Oils from Biomass: Producing, Analyzing, and Upgrading*; Soltes, E. J., Milne, T. A., Eds.; ACS Symposium Series 376; American Chemical Society: Washington, DC, 1988; pp 113−118.

(19) Elliott, D. C.; Hart, T. R.; Neuenschwander, G. G. Chemical processing in high-pressure aqueous environments. 8. Improved catalysts for hydrothermal gasification. *Ind. Eng. Chem. Res.* **2006**, *45*, 3776−3781.