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Hydrothermal carbonization of microalgae

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ABSTRACT

Hydrothermal carbonization is a process in which biomass is heated in water under pressure to create a char product. With higher plants, the chemistry of the process derives primarily from lignin, cellulose and hemicellulose components. In contrast, green and blue-green microalgae are not lignocellulosic in composition, and the chemistry is entirely different, involving proteins, lipids and carbohydrates (generally not cellulose). Employing relatively moderate conditions of temperature (ca. 200 °C), time (<1 h) and pressure (<2 MPa), microalgae can be converted in an energy efficient manner into an algal char product that is of bituminous coal quality. Potential uses for the product include creation of synthesis gas and conversion into industrial chemicals and gasoline; application as a soil nutrient amendment; and as a carbon neutral supplement to natural coal for generation of electrical power.

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1. Introduction

With the apex of the world's petroleum production from known reserves having already been achieved or will be attained in the very near future, increased utilization of coal as an energy source seems a certainty. Aside from formidable health problems associated with increased atmospheric particulate and heavy metal contents, coal, like petroleum, is a fossil fuel and burning massively increased quantities of coal will greatly exacerbate the very serious problem of global warming. In contrast, combustion of biomass that has not been stored for eons in subterranean reservoirs releases carbon dioxide that is not "new" to the earth's atmosphere and constitutes a "carbon neutral" event.

Green and blue-green (cyanobacteria) microalgae have been on the earth for millions of years and differ substantially from higher plants. They are single-celled microorganisms that live in aquatic environments, and all components necessary for life and procreation are located within a single cell. In higher terrestrial plants, specialized cells with specific functions are required that make up roots, stems, flowers and other functional parts. Cellulose, hemicellulose and lignin often provide structural support for these specialized cells and are present in significant quantities. In contrast, microalgae and cyanobacteria are not lignocellulosic in composition but are comprised of proteins, lipids, non-cellulosic carbohydrates, and nucleic acids.

Various hydrothermal processing methods have been reported. All enjoy the significant advantage that starting

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biomass does not need to be dry, and the significant energy input required to remove water by evaporation is eliminated. Hydrothermal gasification is the most thermally severe and has been conducted both without catalyst at 400–800 °C [1] and in the presence of Ni and Ru catalysts at 350–400 °C [2]. Gaseous products include hydrogen, methane, and carbon dioxide, and this process has also been extended to microalgae [3]. Hydrothermal liquefaction, generally conducted at 250–450 °C [4], provides liquid bio-oils as well as gaseous products and has also been extended to microalgae [5].

The mildest reaction conditions in terms of temperature and pressure are employed in hydrothermal carbonization (HTC). Lignocellulosic substrates have been extensively examined [6] as reactants at temperatures from 170 to 250 °C over a period of a few hours to a day, and this process has been the subject of a recent tutorial review [7]. The process takes place effectively only in water, is exothermic, and proceeds spontaneously. Two product streams are created that are isolated by filtration: 1) an insoluble, char product and 2) water soluble products. In general, the desired objective of increasing the carbon-to-oxygen ratio (commonly referred to as “carbonization”) has been accomplished by endeavoring to split off carbon dioxide [8–10]. This mechanism is undesirable because, with loss of carbon dioxide, carbon is depleted as well as oxygen, and creation of gaseous products causes even greater reaction pressures that increase complexity/cost of reaction equipment. No published technical reports of algal species being subjected to HTC have been found.

The principal objective of the present work was to focus on the char product and to obtain a high level of carbonization and yield, while simultaneously minimizing processing time. Hopefully, relatively brief reaction times can be employed in a batch mode that would suggest the potential for continuous processing. This is regarded as being imperative if the technology is to have longer term practical impact. Microalgae should be excellent biomass substrates for this purpose because their small size will facilitate rapid thermal transfer to processing temperatures. A secondary objective was to accomplish carbonization by a mechanism other than by loss of carbon dioxide, and the non-cellulosic carbohydrate composition of microalgae may allow dehydration to occur at relatively moderate temperatures in the manner of soluble biomass substrates, e.g., glucose [11]. Reaction parameters examined included time, temperature, and algal concentration. Potential catalysts for the HTC process with microalgae were also evaluated. Compositions and energy contents of resulting algal char products were determined and compared with a natural coal and a char obtained by HTC of a lignocellulosic biomass substrate.

2. Experimental

2.1. Material and methods

Elemental analyses, heats of combustion, ash, and carbonate determinations for the various products were performed by Galbraith Laboratories, Inc. (Knoxville, TN). SEM analyses were performed at the University of Minnesota Imaging Center, College of Biological Sciences, St. Paul, MN.

2.1.1. Algae

Chlamydomonas reinhardtii (CC-125 wild type mt+137c) was obtained from The Chlamydomonas Resource Center (supported by the National Science Foundation) at the University of Minnesota. The alga was inoculated into 20 L glass carboys containing 18 L of TAP medium [12]. *Synechocystis* sp. strain PCC 6803 [N-1] was obtained from the American Type Culture Collection (Manassas, VA) and used to inoculate a 20 L glass carboy containing 18 L of BG-11 medium [13]. The inoculated carboys were placed within fluorescent light rings, producing 5960 cd and sparged with air containing 5% carbon dioxide for several days until the cell count reached a plateau as determined using a hemocytometer. Algae were harvested by centrifugation (8000 × g at 22 °C for 15 min). When crossflow filtration was employed, the alga was resuspended in 1 L of water and diafiltered against 8 L of water by passage through an Amersham Biosciences CFP-2-E-5A Hollow Fiber Cartridge using a peristaltic pump and a flow rate of 10 L/min. Centrifugate pastes were freeze-dried in order to employ accurate and reproducible masses in experiments. *Aphanizomenon flos-aquae* was purchased from Klamath Lake, Inc. (Klamath Falls, OR). *Spirulina* spp. and *Chlorella* spp. were both purchased as food-grade materials from a local health food store; the spray-dried materials were utilized as received. *Dunaliella salina* containing 2% β-carotene was a food-grade product obtained from Alibaba Inc. and was used as received.

2.1.2. Other materials

Oxalic acid, citric acid, and metal salt additives were purchased from Aldrich Chemical Inc. (Milwaukee, WI) and Alfa Aesar (Ward Hill, MA).

2.1.3. Reactor

The reactor employed was a 450 mL stirred stainless steel reactor purchased from Parr Instruments, Inc. (Moline, IL). Heating was applied to the reactor using an induction heating system (available from LC Miller, Co., Monterey Park, CA).

2.2. Hydrothermal carbonization reactions

2.2.1. Algal reactions exemplified with *C. reinhardtii* (7.5% solids, 2.3 wt% oxalic acid, 203 °C, 2 h)

Freeze-dried *C. reinhardtii* (16.2 g), oxalic acid (0.37 g; 2.3 wt%), and 200 mL of distilled water were transferred into a 500 mL round-bottomed flask and shaken vigorously. To ensure that the material was dispersed adequately, the contents were poured into a blender and agitated at high speed for 1 min. The contents were then poured into the 450 mL reactor, with 208.4 g (96%) being transferred. While stirring at 60 rpm, the autoclave was heated inductively to 203 °C for 2 h. Final pressure was 1.65 MPa. After cooling to room temperature (22 °C) overnight, the residual pressure was 0.41 MPa. Gas in the headspace of the reactor was released into a Tedlar gas collection bag and analyzed using a Prima δB Quadrupole Mass Spectrometer (available from Thermofisher, Vernon Hills, IL) using Gasworks Software (version 2.0). Carbon dioxide was the predominant gas, with some carbon monoxide also being detected. Ammonia gas was not distinguishable by this method. Vacuum filtration of the reaction mixture separated the blackened char product from the water

soluble products. The filtered solid was washed well with water and freeze-dried. The char product weighed 6.15 g (39% mass yield based on alga charged). The char and freeze-dried starting alga were submitted for elemental analysis and heat of combustion determination: starting *C. reinhardtii*, %C = 51.6, %H = 7.9, %N = 9.8, %S = 0.6 and heat of combustion = 18.04 MJ kg⁻¹; algal char from *C. reinhardtii*, %C = 72.7, %H = 9.7, %N = 5.2, %S = <dl and heat of combustion = 31.58 MJ kg⁻¹.

2.2.2. With a lignocellulosic prairie grass (Little Blue Stem)
Little Blue Stem [*Schizachyrium scoparium* (Michx.) Nash] grown in monoculture was received from C. Lehman in the Department of Ecology, Evolution & Behavior at the University of Minnesota. The material was thoroughly dry and brown in color. The grass had a lignin content of 20% and a polysaccharide content derived from the following monosaccharides obtained on hydrolysis and listed in decreasing quantity: glucose, xylose, galactose, arabinose and mannose. The dried material was initially ground using a Wiley mill, then a Thomas mill employing a 0.05 mm screen. The resulting fine powder contained particles with a length axis of about 1 mm. Into a 500 mL round-bottomed flask were charged 29.25 g of the finely divided grass, 0.67 g of oxalic acid, and 263 mL of distilled water (achieving a 10% solids concentration). This was transferred (97% transfer) into the 450 mL reactor and allowed to stir (60 rpm) and hydrate overnight. Heating to 200 °C was conducted using a heating mantle for 17 h. When cool, the residual pressure was 0.69 MPa and the mixture was vacuum filtered. The filtrate was clear and yellow in color. The filtered solid was washed well with water, frozen at -20 °C and freeze-dried. The somewhat fibrous, brown filtered product weighed 16.29 g (57% yield based on grass charged). Analysis of the starting prairie grass: %C = 46.6, %H = 6.2, %N = <0.5% and heat of combustion = 17.92 MJ kg⁻¹. Analysis of the lignocellulosic char: %C = 62.3, %H = 5.6, %N = <0.5% and heat of combustion 24.38 MJ kg⁻¹.

3. Calculations

Computations for the following sections were conducted using experimental details of the HTC of *C. reinhardtii* of Section 2.2.1.

3.1. Comparison of energy input/output for combustion of *C. reinhardtii* and its algal char product (Section 4.3.2)

3.1.1. Combustion of *C. reinhardtii*

The centrifugate paste had an algal concentration of 10 wt%, and 10 kg of paste were considered in the computations. From Steam Tables [14], in order to remove 9 kg of water from 10 kg of paste:

$H_{\text{steam @ 373 K}} - H_{295 \text{ K}} = 2.68 - 0.09 = 2.59 \text{ MJ kg}^{-1}$. For 9 kg of water the energy required is $9 \times 2.59 = 23.31 \text{ MJ}$. Heat of combustion of the dry alga = 18.04 MJ kg⁻¹, and the overall energy balance is a net loss of $18.04 - 23.31 = -5.27 \text{ MJ}$.

3.1.2. Combustion of algal char from *C. reinhardtii*

Step 1: Heat 10 kg of centrifugate paste from 295 K to 476 K under pressure with no vaporization in the pressurized system: Enthalpies of saturated liquids (h_f) = 0.86 MJ kg⁻¹ at 476 K and 0.09 MJ kg⁻¹ at 295 K; $\Delta h_f = 0.86 - 0.09 = 0.77 \text{ MJ kg}^{-1}$; assuming the heat capacity of the 1 kg of dry alga present to be about 50% that of water: $\Delta H_{\text{step 1}} = 0.77 (9 \text{ kg}) + 0.5 (0.77) (1 \text{ kg}) = 7.31 \text{ MJ}$.

Step 2: Filter 10 kg of wet algal char to obtain 0.63 kg of moist char and 9.37 kg of filtrate: No significant energy input.

Step 3: Dry the 0.63 kg of moist algal char to remove 0.23 kg of water at 373 K: $\Delta H_{\text{vaporization}} = 2.26 \text{ MJ kg}^{-1}$, and for $0.23 \text{ kg} \times 2.26 \text{ MJ kg}^{-1} = 0.52 \text{ MJ}$.

Total heat load for 0.4 kg of dry algal char: $7.31 + 0.52 = 7.83 \text{ MJ}$.

Total heat load for 1.0 kg of dry algal char: $7.83 \div 0.4 = 19.57 \text{ MJ}$, and the overall energy balance is a net gain of $31.58 - 19.57 = +12.01 \text{ MJ}$.

3.2. Carbon accounting (for Section 4.3.3)

3.2.1. Reactant

Freeze-dried starting alga weight (Section 2.2.1) = 15.55 g (actually transferred into the reactor) having a %C = 51.9, providing 8.07 g of carbon in the starting alga substrate.

3.2.2. Products

Freeze-dried algal char weight = 6.15 g having a %C = 72.7, providing 4.47 g of carbon or 55% of the starting carbon in the char product. The aqueous filtrate volume was 192 mL and had a % solids = 3.94; the brown solid solutes weighed 7.56 g and possessed a %C = 48.1 (carbonate analysis was <0.03%), providing 3.64 g of carbon in the aqueous filtrate or 45% of the starting carbon. Assuming all the gas in the headspace of the reactor was carbon dioxide, the pressure at 22 °C (295 K) was 0.41 MPa + 0.10 MPa = 0.51 MPa and occupied ca. 250 mL. Applying the Universal Gas Law (rearranged to compute the number of moles of carbon dioxide) with the appropriate constant ($R = 8.31 \text{ mL MPa K}^{-1} \text{ mol}^{-1}$):

$$\begin{aligned} \text{Number of moles} &= \text{pressure} \times \text{volume} \div R \\ &\times \text{Temperature (295 K)} = (0.51)(250) \div (8.31)(295) \\ &= 0.05 \text{ mole of carbon dioxide having} \\ &\quad \text{a molecular weight of 44 g/mole} \\ &\quad \text{and \%C} \\ &= 27.3 \text{ which computes to 0.60 g of} \\ &\quad \text{carbon in the carbon in the} \\ &\quad \text{headspace} \end{aligned}$$

Calculation of the amount of carbon dioxide dissolved in the 192 mL of water at 22 °C (solubility of carbon dioxide in water at 22 °C = 0.16 g/100 g at 1 atm [15]) provides 0.31 g @ %C = 27.3 or 0.08 g of carbon dissolved in the water. The combined quantity of carbon dioxide in the headspace and dissolved in the water was 0.68 g or 8% of the starting carbon.

4. Results and discussion

4.1. Effect of metal salt additives and acids

An early report [16] examining the hydrothermal carbonization of sucrose focused on the development of turbidity in the presence of various metal salt additives at 100–120 °C. Of the metal salts reported to have a high degree of influence on turbidity development, only CaCl₂ and MgCl₂ were environmentally acceptable as additives; oxalic acid was also reported to be highly effective. Another report [17] indicated that ferrous ion and iron oxide nanoparticles were effective catalysts in HTC of insoluble biomass. These additives and citric acid were examined with *D. salina* at 15% solids, 200 °C, and for 2 h; additive concentration in all cases was 0.54 mol percent which was equivalent to 2.0 wt% of CaCl₂ examined in the initial additive experiment. Carbonization levels as indicated by %C values were essentially the same in all cases including a control experiment with no additive. Similarly, % mass yields ranged from 37 to 40%. Therefore, no clearly superior additives were identified that gave significantly increased levels of carbonization or mass yields. However, since an acidic pH had been reported [6] to provide less carbon dioxide product, either citric or oxalic acid (2–3 wt%) was added in subsequent experiments.

4.2. Designed experiment with *D. salina*

D. salina was of particular interest because it can grow well in water containing relatively high concentrations of dissolved salts. In this environment, predatory effects of bacteria are greatly reduced, and expensive sterilization measures are not required for algal production. In order to examine the importance and interdependence of suspected key variables, a three-variable, two-level factorial experiment with replicated centerpoints was conducted. Variables of temperature, time and algal concentration were examined simultaneously. Temperatures examined were: 190, 200, and 210 °C; reaction times: 0.50, 1.25, and 2.00 h; and % solids levels: 5, 15, and 25% alga by weight. The results are given in Table 1.

A linear regression equation was developed from the orthogonal factorial design:

$$\% \text{ Carbon Recovered} = 51.54 - 1.375X_1 - 0.375X_2 + 9.875X_3$$

where X_1 = dimensionless temperature; X_2 = dimensionless time; and X_3 = dimensionless % solids.

Analysis of variance (ANOVA) showed that % solids was significant at the 99% confidence level, and temperature was significant at the 95% confidence level. Time was not statistically significant which has positive implications for scaling from batch to continuous processing methods by employing reaction times even less than 30 min. Further statistical analysis indicated that the simple linear model did not explain all the variation in the experimental data. The significant interaction between temperature and time at the 95% level indicated a non-linear response surface.

Overall, these results suggested that the processing window was relatively wide. The data of Table 1 are

Table 1 – Designed experiment examining the effects of reaction temperature, time, and algal concentration.

Temp. (°C)	Time, h	% Solids	% Mass yield	% Carbon recovered ^a in the algal char product
190	0.5	5	28.4	40
190	0.5	25	45.7	62
190	2.0	5	29.3	40
190	2.0	25	42.9	61
200	1.25	15	39.3	55
200	1.25	15	39.0	56
200	1.25	15	37.4	55
200	1.25	15	38.1	55
210	0.5	5	27.9	40
210	0.5	25	42.1	60
210	2.0	5	25.3	38
210	2.0	25	38.8	57

^a This value was computed by dividing the amount of carbon in the char (%C times the mass of char) by the amount of carbon in the starting alga (%C times mass of alga).

depicted graphically in Fig. 1A–C. Fig. 1A is a plot of % carbon recovered in the algal char at different temperatures and times, and darker colored regions represent higher % carbon yields. The topographical response surface is fairly “flat” in that not much is changing with regard to these two input variables. By contrast, Fig. 1B and C that involve algal concentration (% solids) with temperature and time, respectively, show considerable change occurring in both plots due to the significant importance of concentration of the alga. Furthermore, Fig. 1B and C indicate that an undesirable “over cooking” is indicated both at the highest reaction temperature and longest reaction time. These observations suggest that continuous processes might be developed by employing even higher % solids at temperatures of less than 200 °C with reaction times of less than 30 min to provide acceptable char products in terms of carbonization and yield.

4.3. Summary evaluation of green and blue-green microalgae in HTC

Several strains of algae were examined for char production under a variety of experimental conditions. Elemental analyses of both starting freeze-dried alga and algal chars are given in Table 2 for comparison.

One observation from the table was that useful carbonization levels in chars derived from blue-green bacteria could be obtained, e.g., with *Aphanizomenon flos-aquae* and *Synechocystis*, but the yields of chars were significantly lower than those obtained with green microalgae. This may be attributed to the reduced strength of a bacterial cell wall relative to a plant cell wall and that the contents of the bacteria were more extensively lysed, possibly providing less material available for char formation. Cell wall composition may not be the only factor influencing formation of char, however, as *D. salina* that does not possess a cell wall but only a cell membrane of mostly lipid composition [18]

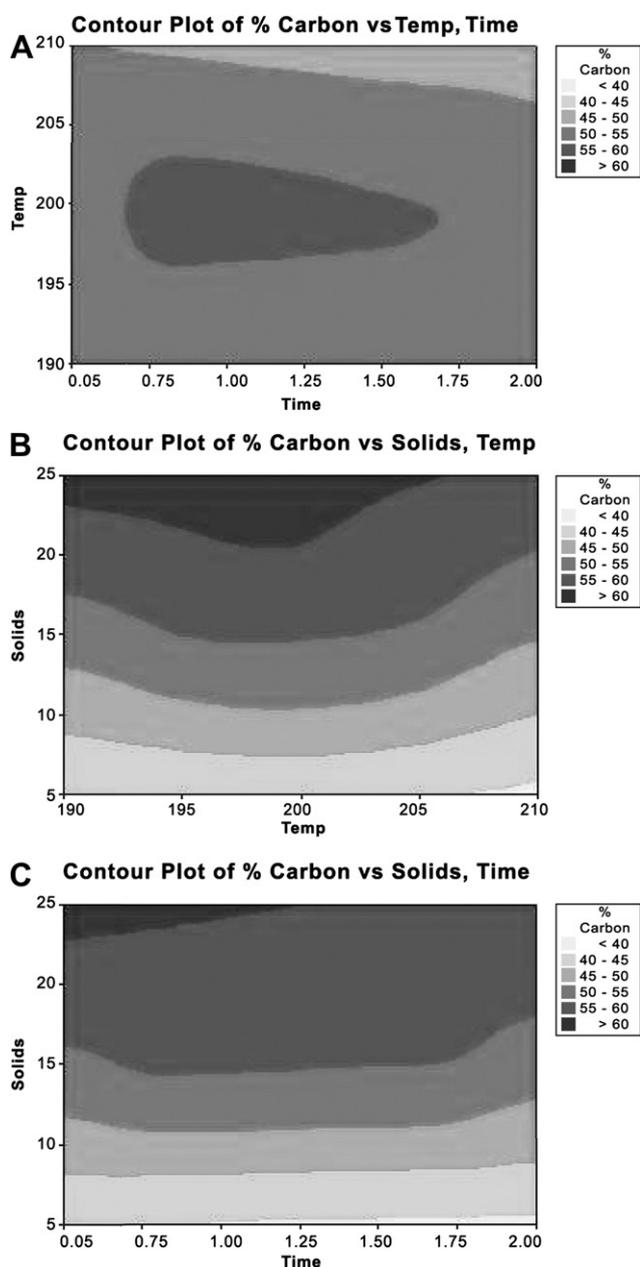


Fig. 1 – Contour plots of % Carbon Recovered versus time, temperature (A), % solids, temperature (B) and % solids, time (C).

provided a char with a high degree of carbonization and in good yield.

4.4. Algal chars compared with coal and a lignocellulosic char

This section is devoted to comparison of the chars obtained from *C. reinhardtii* as described in Section 2.2.1 and from *D. salina* prepared at 15% solids, 200 °C, 3 h, with 2.3% oxalic acid. The natural coal was a Powder River Basin Coal obtained as a pulverized powder from Xcel Energy, Inc. (St. Paul, MN). The lignocellulosic char was the product from the prairie grass of Section 2.2.2.

4.4.1. SEM comparisons

The images shown in Fig. 2 for natural coal revealed a material that was synthesized in a compressive mode, under substantial pressure and heat with only a somewhat flaky surface appearance evident at high magnification. The char prepared from Little Blue Stem prairie grass had considerable resemblance to the starting prairie grass (not shown). This may be attributed to the cellulose content of the starting biomass that remained unaffected by HTC conditions since reaction temperatures were <220 °C [19]. Char derived from *C. reinhardtii*, on the other hand, was conceivably formed by initial lysis of cells, carbonization of components in solution (or at least in a liquefied state), and agglomeration into larger particles by binding onto whatever solid structures remained in the suspension. As a result, the algal char possessed a more tortuous surface appearance at high magnification.

4.4.2. Comparison of the elemental analyses, heats of combustion, and ash values of natural coal, char from a lignocellulosic substrate, and algal chars obtained from *C. reinhardtii* and *D. salina*

In Table 3 the %C values for the algal chars and the natural coal material were comparable and in the 66–73% range, while only 62% C was observed with the lignocellulosic char despite the extended reaction period of 17 h. Heats of combustion were greatest with the algal chars which indicated the importance of not only of carbon but also hydrogen for energy content, since the algal chars possessed significantly increased amounts of hydrogen than either natural coal or lignocellulosic char. Nitrogen was an insignificant component of both natural coal and lignocellulosic char and suggested that natural coal probably originated predominantly from lignocellulosic vegetation. In the algal chars, however, higher levels of nitrogen were observed and may a negative issue if combustion conditions favor formation of oxides of nitrogen. On the positive side, the very low ash value of char derived from *D. salina* may be a significant attribute if the chars are utilized as a carbon source for conversion into synthesis gas.

Considering the most basic use for algal char, i.e., burning it for its energy content, a comparison of energy outputs for burning *C. reinhardtii* itself and the char derived from it are each summarized in Table 4 (Calculations Section 3.1). Note that the starting point for each material was the centrifugate at 10 wt% concentration.

One major issue with any industrial process involving the combustion of algae is removal of water. In the table, in order to obtain 1 kg of dry alga from a centrifugate at 10% solids, 9 kg of water were required to be removed from 10 kg of the centrifugate. This required 23.31 MJ and resulted in a net energy input into the system of 5.27 MJ. In contrast with the HTC process, the 10% solids concentration was the desired HTC reaction medium and no energy input was initially required. To heat the system from ambient to 203 °C, 7.31 MJ were required, and with proper insulation and temperature control, no significant additional energy was needed to maintain reaction temperature for 2 h. The char product isolated by filtration was moist and required 0.52 MJ to obtain 0.4 kg of dry char. The overall net result was that the process liberated 12.01 MJ kg⁻¹ which was an improvement of 17.28 MJ over burning the starting alga. It

Table 2 – Results of HTC conditions using several algal materials.

Alga	HTC conditions	%C	%H	%N	Yield	% Carbon recovered in char product
Starting AF	–	48.1	7.4	11.5	–	–
Algal Char	5% solids; 213 °C; 2 h	62.7	8.5	7.1	16	21
Starting Syn.	–	48.2	7.3	9.1	–	–
Algal Char	5% solids; 213 °C; 2 h	67.3	9.1	5.5	18	25
Starting Spir.	–	44.4	6.2	7.3	–	–
Algal Char	15% solids; 213 °C; 3 h	58.4	6.7	6.6	27	35
Starting Chlor.	–	50.8	7.2	10.1	–	–
Algal Char	12.5% solids; 200 °C; 3 h	65.3	8.5	7.2	39.5	51
Starting Dunal.	–	45.9	6.3	7.9	–	–
Algal Char	15% solids; 200 °C; 3 h	66.3	7.9	7.3	36	52
Starting Chlamy	–	51.6	7.9	9.8	–	–
Algal Char	7.5% solids; 200 °C; 2 h	72.7	9.7	5.2	39	55

AF = *Aphanizomenon flos-aquae*; Syn. = *Synechocystis spp.*; Spir. = *Spirulina spp.*; Chlor. = *Chlorella spp.*; Dunal. = *Dunaliella salina*; and Chlamy = *C. reinhardtii*.

should also be mentioned that no recovered heat was considered in this hypothetical process, and heat conservation measures would most certainly be employed in any industrial process resulting in additional energy improvement.

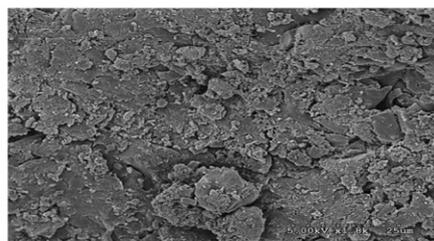
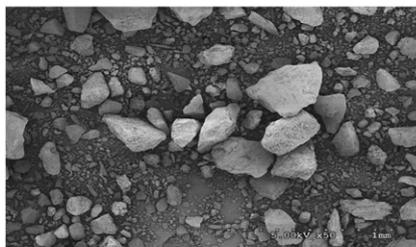
4.4.3. Carbon accounting in the algal char

If the claim is valid under the experimental conditions that carbonization was not achieved by loss of carbon dioxide, it

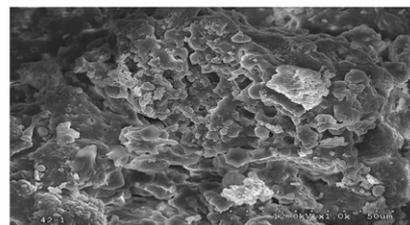
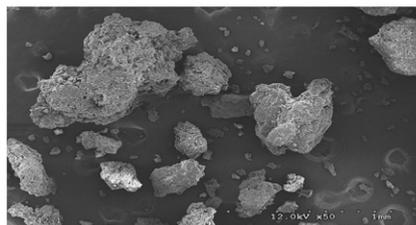
was important to understand how carbon was distributed among the products of the reaction (Calculations Section 3.2). Fig. 3 summarizes the carbon accounting.

Carbon was distributed as follows: 55% in the algal char, 45% in freeze-dried solutes in the aqueous filtrate, and 8% as carbon dioxide present in the headspace of the reactor (assuming all the gas was carbon dioxide) and dissolved in the filtrate. A significant amount of carbon was present in the solutes in the filtrates, and an important question was

Natural coal



Algal Char



Lignocellulosic char from prairie grass

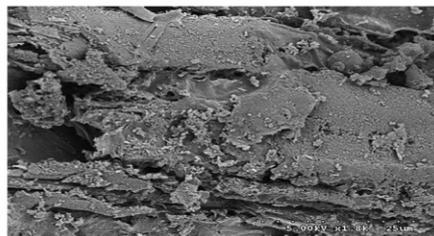


Fig. 2 – SEM pictures of natural coal, algal char and char from a lignocellulosic material.

Table 3 – Elemental analyses, heats of combustion and ash contents of natural coal, lignocellulosic char and algal chars.

Sample	Elemental Analyses				Heat of Combustion (MJ kg ⁻¹)	Wt.% Ash
	%C	%H	%N	%S		
Natural Coal	69.6	5.7	0.9	0.6	28.59	5.60
Lignocellulosic Char	62.3	5.6	<0.5	<0.5	24.38	n.d.
Algal Char ^a	72.7	9.7	5.2	<0.5	31.58	n.d.
Algal Char ^b	66.3	7.9	7.3	0.5	30.51	0.33

a Product obtained from HTC of *C. reinhardtii*.
b Product obtained from HTC of *Dunaliella salina*.

whether a significant concentration of carbonate ion was present that could be derived from carbon dioxide. This was shown not to be the case, as analysis of the filtrate indicated <0.03% carbonates were present. One possible explanation for the significant amount of carbon found in the freeze-dried solutes may be due to Maillard reaction products and the carbon contained therein. This reaction has been reported [20] to create literally hundreds of heterocyclic compounds that would be soluble in water or be adsorbed onto nanoparticles of carbonized material present in the aqueous filtrate that would essentially pass through a conventional filter.

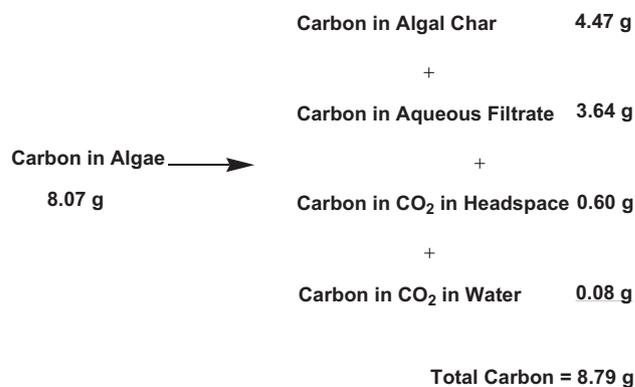
An important conclusion regarding carbonization mechanism that can be made from this study was that a proper tally of carbon dioxide was obtained. Even assuming that all the gaseous products in the headspace of

Table 4 – Energy outputs from the combustion of starting alga and algal char.**Dry *C. reinhardtii***

- Heat of Combustion of freeze-dried *Chlamy* = 18.04 MJ kg⁻¹.
- Alga can be collected by centrifugation @ 10% solids.
- In 10 kg of collected alga, there are 1 kg of alga and 9 kg of water.
- To obtain the dry 1 kg, 23.31 MJ are required to remove the water.
- Therefore, the net energy is a loss of 18.04 – 23.31 = -5.27 MJ.

Dry Algal Char from *C. reinhardtii*

- Heat of Combustion of Algal Char from *Chlamy* = 31.58 MJ kg⁻¹ obtained in 40% yield.
- Alga can be collected by centrifugation @ 10% solids and used directly for HTC.
- To heat the suspension from 22 °C (295 K) to 203 °C (476 K), 7.31 MJ are required. Reaction temperature can be maintained at 203 °C for 2 h without significant additional energy input. Since the products of the reaction are cooled gradually after reaction and not allowed to flash, there is no loss of energy content due to vaporization.
- The filtered char product weighs 0.63 kg and is 63% solids, and 0.52 MJ are required to dry it.
- For the 0.4 kg, 7.31 + 0.52 = 7.83 MJ which is 19.57 MJ kg⁻¹.
- Therefore, the net energy is a gain of 31.58 – 19.57 = +12.01 MJ.

**Fig. 3 – Disposition of carbon in HTC products with *Chlamydomonas reinhardtii*.**

the reactor and dissolved in the aqueous filtrate were carbon dioxide, the level of that product was less than 10% of the total products. The most reasonable alternative explanation, though not directly proven, was that the predominant mechanistic pathway for carbonization was dehydration. Another explanation, though believed less probable, was that the oxygen content was increased in solutes present in the filtrate (and therefore removed from the carbonized char) by fragmentation reactions of carbohydrate polyol materials present in the lyzed alga and formation of water soluble oxidized products such as carboxylic acids, ketones and aldehydes. Clarification of reaction mechanism awaits further investigation.

Table 5 – Comparison of algal char and natural coal.

- **Global Warming Impact:** The burning of natural coal, a fossil fuel, releases new carbon dioxide into the atmosphere. Based on projected growth in coal-fired electricity-generating capacity by 2030, an estimated 2.7 billion tons of new carbon dioxide will be produced annually [21]. Combustion of algal char derived from biomass creates no new carbon dioxide in the earth's atmosphere.
- **Formation:** The conversion of aqueous algal slurries into algal char occurs at a relatively moderate thermal condition in less than an hour under batch processing conditions. Natural bituminous coal, on the other hand, is non-renewable, requiring formation conditions of millions of years of heat and pressure.
- **Isolation:** Algal char is isolated by filtration and obtained as a free-flowing powder. Natural coal is mined thousands of meters below the earth's surface and must be pulverized and powdered before use.
- **Contaminants:** Most natural coal is contaminated with Cl, S, Hg, Pb, Cd, U, Br, Cr, Cu, Fe and Zn [22], some of which contribute to serious health problems when released into the environment. In contrast, algal char has only trace quantities (ppm levels) of environmentally benign S, Cu and Fe.
- **Fuel Quality:** Both products are of bituminous level quality in terms of % carbon and energy content.

5. Conclusions

Hydrothermal carbonization of microalgae provided char products of unique composition and with energy contents in the bituminous coal range. Process conditions were remarkably mild, e.g., ca. 200 °C and times as brief as 0.50 h, for developing acceptable levels of carbonization and yields of algal char materials. The relatively brief reaction time demonstrated in batch processing suggested that a continuous process might be developed for the HTC processing of algae. Some strains of cyanobacteria also provided high quality chars but yields were only half those obtained with green microalgae. No definitive catalytic agents were identified that significantly accelerated carbonization and/or enhanced yield with algal substrates. The fundamental carbonization process was shown to not proceed by loss of carbon dioxide. The most plausible alternative pathway proposed, though not directly substantiated, was carbonization via a dehydration route. Additional important and practical comparisons of natural coal and algal char are contained in Table 5.

An important area of active future work will be to define utility for the aqueous filtrate byproducts. These complex solutions contain considerable quantities of nitrogen-containing solutes and are currently being examined as nutrient materials for both higher plants and algae.

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