Gasification of Phycoremediation Algal Biomass

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Microalgae have been utilized in wastewater treatment strategies in various contexts. Uncontrolled algal species are a cheap and effective remediation strategy. This study investigates the thermochemical potential of wastewater treatment algae (phycoremediation) as a means to produce renewable fuel streams and bio-products. Three gasification temperature levels were investigated in an auger gasification platform: 760, 860, and 960 °C. Temperature increases resulted in corresponding increases in CO and H_2 concentrations in the producer gas from 12.8% and 4.7% at 760 °C to 16.9% and 11.4% at 960 °C, respectively. Condensable yields ranged between 15.0% and 16.6%, whereas char yields fell between 46.0% and 51.0%. The high ash content (40% on a dry basis) was the main cause of the elevated char yields. On the other hand, the relatively high yields of condensables and a high carbon concentration in the char were attributed to the low conversion efficiency in this gasification platform. Combustion kinetics of the raw algae, in a thermogravimetric analyzer, showed three consecutive stages of weight loss: drying, devolatilization, and char oxidation. Increasing the algae gasification temperature led to increases in the temperature of peak char oxidation. Future studies will further investigate improvements to the performance of auger gasification.

Keywords: Algae; Phycoremediation; Gasification; Wastewater treatment; Auger reactor; Char; Condensables; Producer gas yield

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INTRODUCTION

Microalgae are attracting wide interest as a renewable feedstock due to their short life cycle and high photosynthetic efficiency, in addition to the full range of products and services they furnish. Historically, macroalgae and microalgae have been utilized in the production of nutritional supplements, animal feed, cosmetics, and pharmaceuticals (Brown 2002; Del Campo *et al.* 2007). Increased awareness of the consequences of fossil fuels overuse and the resulting emissions have prompted an interest in algae as a renewable energy resource. Algae cultivation as a means for both carbon sequestration and fuel production is among the most exciting technologies in this regard (Sheehan *et al.* 1998; Stewart and Hessami 2005; Chisti 2007). Another service provided by algae that is receiving renewed attention is wastewater treatment, typically referred to as "phycoremediation". The discharge of nutrient-enriched effluent to rivers and lakes from sewage treatment plants and livestock farms has been shown to result in eutrophication and hypoxic conditions (Kemp *et al*. 1983; Valiela *et al.* 1997). Since low phosphorous (P) and nitrogen (N) concentrations are typically the limiting factors of algal blooms in balanced aquatic environments, introducing untreated (nutrient-rich) effluents instigates their growth. Various studies have successfully demonstrated the potential of microalgae as a treatment option for effluent from livestock production (Wilkie and Mulbry 2002; Ji *et al.* 2013) and municipal wastewater treatment plants (Åkerström *et al.* 2014). The N and P uptake by periphytic algal communities grown in an algal turf scrubber system (ATS) was evaluated as a treatment option for a nutrient-rich creek in Northwest Arkansas (Sandefur *et al.* 2011). A mixed algal culture (green, blue-green, diatoms, and flagellates) was evaluated as a scrubber of adsorbable organic halides (AOX), as reported by Dilek *et al.* (1999). These researchers also used this mixture to control color in industrial pulp and paper plant effluent. A mixture of immobilized microalgae and bacteria in polymer matrices (composed of natural and synthesized polymers) has also received attention as another approach that facilitated the assimilation of nutrients and metals while protecting the selected algal strains from invasive species (Hernandez *et al.* 2006; de-Bashan and Bashan 2010).

The quality of wastewater-grown algal biomass has been investigated to evaluate its potential use as a source of high-value chemicals, fuel, and feed. Despite a high protein content in excess of 40% on a dry mass basis, the high levels of heavy metals in wastewater algae can exceed the maximum dietary levels tolerated in livestock, thus reducing the value of wastewater algae as a feed source (Wilkie and Mulbry 2002). Similarly, the increased nitrogen concentration in wastewater was found to reduce the lipid accumulation in algae cellular structures (Li *et al.* 2008). Consequently, the low content of fatty acids in wastewater treatment algae makes them a poor candidate for lipids extraction.

Another algal biomass utilization route is biological digestion. Under mesophilic conditions (35 °C), algae were found to exhibit slow, incomplete degradation and low gas production rates compared to sewage sludge (Golueke *et al.* 1957). A relative improvement in algae digestibility, reported under thermophilic conditions at 50 to 55 °C, was attributed to the partial destruction of cell walls, which improved accessibility to bacteria. Later investigations showed that 40% of the organic fraction in algae was not biodegradable (Jewell and McCarty 1971). Yen and Brune (2007) proposed blending waste paper with algal sludge to adjust the C/N ratio to 20 to 25 and minimize ammonia (NH_3) release during decomposition. A significant increase in methane production was observed after blending, compared to unblended algal biomass: 1170 mL L^{-1} d^{-1}, compared to 573 mL L^{-1} d^{-1}. Algal cell walls' resistance to bacterial degradation, combined with the low C/N ratio in algae between 6 and 9, are often cited as causes of low algae digestibility.

Thermochemical processes, whether under aqueous or dry conditions, offer the flexibility to produce gaseous, liquid, and solid valuable products from algal biomass without the need for metabolic degradation. Combustion, gasification, pyrolysis, and hydrothermal liquefaction processes have been rigorously investigated on a wide variety of feedstocks ranging from wood and crop residues (Scott *et al.* 1985; Van der Drift *et al.* 2001; Sadaka 2013) to industrial and municipal wastes (Xu and Antal 1998; Larson *et al.* 2000) and livestock manures (He *et al.* 2000; Young and Pian 2003; Priyadarsan *et al.* 2004). Bio-crude produced from the hydrothermal liquefaction of *Spirulina* algae has been characterized and compared with bio-crude produced from swine manure and digested sludge (Vardon *et al.* 2011). Few investigations, however, have been carried out to examine atmospheric pyrolysis, gasification, and combustion of microalgae feedstocks. This absence of research can be attributed to the high drying overhead, which diminishes the benefit of thermochemical conversion. Another problem associated with microalgae combustion is the high ash and mineral contents, which result in slagging and fouling. Co-firing microalgae with coal or natural gas has been considered as an environmentally sound investment, with the exhaust CO_2 being utilized to grow the algal biomass cultures (Doucha *et al.* 2005; Ma and Hemmers 2010). Ross *et al*. (2008) studied the thermochemical behavior of a group of marine macroalgae species: *Fucus vesiculosus, Chorda filum,* *Laminaria digitata, Fucus serratus, Laminaria hyperborea*, and *Macrocystis pyrifera*. Ash content for these species ranged between 9% and 18%, which might complicate combustion and gasification. Demirbas (2009) reported the optimal temperature range for pyrolysis oil production in two moss species (*Polytrichum commune* and *Thuidium tamarascinum*) and two algae species (*Cladophora fracta* and *Chlorella protothecoid*) to be 350 to 450 °C. This range is mainly favored because higher temperatures promote further cracking, and consequently, more gaseous products. In another study, steam gasification of char recovered from fast pyrolysis of cyanobacterial blooms was investigated (Yan *et al.* 2010). They reported the particle size to have no effect on gas composition, while the residence time was a significant factor in the gasification process yields. They reported a maximum gas yield (1.84 $Nm^3 kg^{-1}$) and carbon conversion (98.8%) at 850 °C, with a 15 min residence time and a particle size of 0.45 to 0.90 mm.

There appears to be a need for further investigation of the quality of char produced from aquatic biomass gasification, predominantly in an auger reactor. This investigation aims to explore the quality of wastewater microalgae as a feedstock for the gasification process and to study the quality of the char products under various temperatures.

EXPERIMENTAL

Materials

Biomass collection and characterization

In this study, algal biomass was harvested from a pilot-scale shallow raceway at Paul R. Noland Wastewater Treatment Plant (Fayetteville, AR). The algal species grown in that system and investigated in this study are essentially mixtures of indigenous uncontrolled aquatic species (algae and diatoms). Harvesting was accomplished manually by scraping the carpeted bedding of the raceway, then straining the harvested biomass on a large screen to remove free water. Aquatic biomass was collected in plastic airtight containers and stored at 0 °C prior to preparation and analysis. The algal biomass used was compiled from harvests during June, July, and August of 2011. The biomass was oven-dried at 80 °C, until weight loss was minimal, to avoid significant losses of volatile matter. Dried biomass was then pulverized using a 1.5 hp (1.1 kW) grinder (Model No.3, Wiley Mill, Swedesboro, NJ). Proximate analyses were performed according to standard procedures, *i.e.*, moisture content (ASTM E871-82 2006), volatile matter (ASTM E872-82 2006), and ash content (ASTM D2974-8 2007). Fixed carbon, on the other hand, was determined by subtraction of these first three values from the maximum possible, 100%. The elemental analysis was performed in a specialized diagnostic laboratory (Huffman Laboratories Inc., Golden, CO). Sample carbon, hydrogen, and nitrogen contents were determined according to standard ASTM D5373-14, while sulfur was determined using standard ASTM D4239-14e1. The elemental analysis of the ash oxides was quantified according to standard ASTM 6349 (2013). The higher heating value (HHV) of algae samples was determined using oxygen bomb calorimetry (model 1241; Parr Instruments, USA) (ASTM D5865-12 2012). The chemical oxygen demand (COD) of the dried raw algal biomass and the gasification chars was determined by first diluting each solid sample with deionized water (100 g water per 1 g solids). The suspensions were then thoroughly homogenized and left to settle for 30 min. The suspension was then filtered, and a 2-mL aliquot of the filtrate was added to the COD digestion vial (0 to 15,000 ppm range). A digital reactor block (DRB200; Hach Company, Loveland, CO) was used to digest each sample at 150 °C for 2 h. After cooling the samples to below 120 °C, the COD was determined using a portable spectrophotometer (DR 2700, Hach Company).

Methods

Auger gasification system

Atmospheric air gasification tests were conducted in an auger gasification/ pyrolysis system. This system was designed and constructed in the bioenergy laboratory at the Rice Research and Extension Center (Stuttgart, AR). Figure 1 shows a schematic diagram of the gasification system used. Preliminary results of this investigation were reported by Sharara and Sadaka (2012). The reactor is essentially an externally heated cylindrical reactor (Type 316 stainless steel): 1.32 m long, 0.06 m inside diameter, and 0.005 m wall thickness. Motorized augers were used to move the feedstock from the hopper and through the reactor. A three-zone electrical heater (Model HTF55347C, Lindberg/Blue M, Asheville, NC), each zone is 0.20 m long, is used to heat the reactor. The heated section starts 0.45 m from the biomass drop-off point into the auger reactor. The feeding rate was controlled by adjusting the rotational speed of the injection (metering) auger, as shown in Fig. 1. Multiple calibrations were performed using the ground algal biomass prior to actual gasification tests to accurately adjust the biomass feed rate and determine the biomass fullness ratio (α), which represents the percentage of the auger cross-sectional area occupied by the biomass. Table 1 summarizes the parameters of the three gasification tests reported in this study.

Table 1. Parameters of Algae Gasification Tests

Test	1	2	3
Furnace Temperature (°C)	760	860	960
Auger speed (rpm)	6.02	6.20	6.32
Biomass feed rate (g min^{-1})	34.7	36.1	40.9
Air flow rate (L min^{-1})	20.0	20.0	18.1

All tests were initiated after the furnace temperature and the temperatures inside the reactor became constant. Each test lasted 15 min, during which time the gas was sampled for 10 min after 5 min had passed since initiating the feeding. Tar and char produced after each test were collected, weighed, and stored for further analyses. After exiting the tar collection unit, the producer gas was cooled and cleaned using a tar trap lined with glass wool. The flow rate of the cleaned producer gas was then measured using a 5-VDC volumetric air flowmeter (Omega, FLR1000 series; USA). Producer gas composition was determined using a 5-gas analyzer (O_2, CO, CO_2, H_2, and CH_4) (Model 7905AQ, Nova Analytical Systems; USA). In this study, however, the methane concentration was not reported due to interference from other produced hydrocarbons that significantly influenced methane readings.

Thermogravimetric analysis

The oxidation behavior of the raw algal biomass, as well as the algae gasification chars, was investigated using thermogravimetry. The dry samples were first milled and sieved to generate a sub-sample with a particle size less than 0.2 mm. A thermogravimetric analyzer (Model TGA 4000, Perkin Elmer, Inc., Waltham, MA) was used to determine the relationship between temperature and weight loss for the different samples under oxidizing conditions. Simulated air was used as the purge gas at a flow rate of 50 mL min^{-1} and a heating rate of 5 °C min^{-1}. The sample weight was maintained at 5 mg (± 0.1 mg) in all the TGA tests. Both the particle size and the sample size were kept sufficiently small to ensure that the decomposition was controlled by kinetics rather than diffusion. Each sample was placed in a clean, inert alumina (Al_2O_3) crucible. A blank test was conducted with an empty crucible under the regular test conditions to quantify the buoyancy of the crucible. The experimental data was then corrected by subtracting the blank test results.

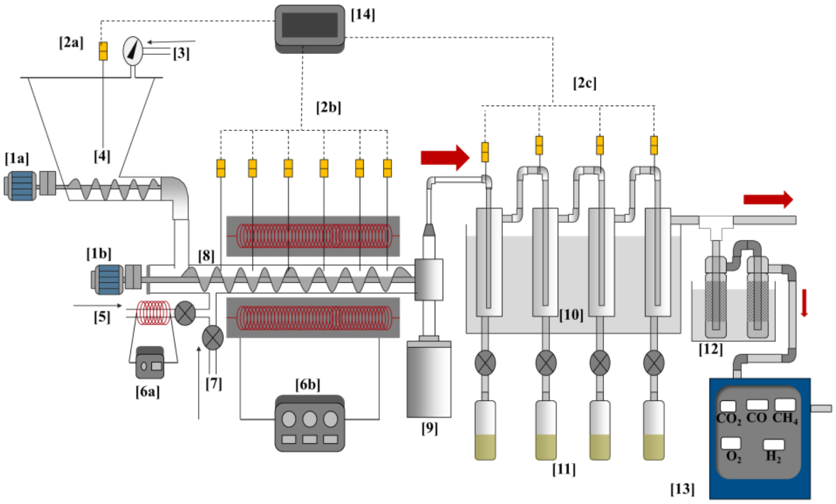

Fig. 1. Schematic of auger gasification/pyrolysis reactor. 1a, 1b. Controllable DC motors; 2a, 2b. 2c. Type-K Thermocouples; 3. Nitrogen purge; 4. Injection/metering auger; 5. Auxiliary steam feed; 6a, 6b. Controllable heaters; 7. Oxidant feed (air); 8. Auger reactor; 9. Char collector; 10. Condensers assembly; 11. Tar collection bottles; 12. Gas wash bottles; 13. Permanent gases analyzer; and 14. Data logging unit.

RESULTS AND DISCUSSION

Temperature Profile

In addition to the thermocouples controlling the furnace temperature based on the reactor's external temperature, five thermocouples were installed to measure the biomass temperature inside the reactor. In the three gasification tests, a shift in the temperature profile was observed after biomass feeding was initiated. The first half of the externally heated auger reactor, *i.e.*, at a length less than 0.6 m, underwent a gradual drop in temperature, as shown in Fig. 2, while temperatures further along the reactor showed a gradual increase. Nominal gasification temperatures, *i.e.*, 760, 860, and 960 °C, were maintained in the reactor section directly surrounded by the heating element. Before biomass feeding, the temperature profile was determined primarily by the set temperature of the heating element, proximity to the heating element, and the heat transfer affected by the gasifying agent. After feeding, however, typical gasification stages took place consecutively along the reactor length: drying, devolatilization (pyrolysis), oxidation, and partial oxidation. Both drying and devolatilization, which are endothermic reactions, took place at the beginning of the reactor, while oxidation and partial oxidation, both exothermic reactions, took place toward the end of the reactor. This sequence of stages could explain the observed temperature profile changes after biomass feeding was initiated. Similar thermal stratification has been observed in fixed-bed gasification reactors, *i.e.*, updraft and downdraft reactors (Zainal *et al.* 2002). Fixed-bed reactors are known for their ease of operation, but they typically result in higher tar yields than fluidized-bed gasifiers (McKendry 2002; Warnecke 2000).

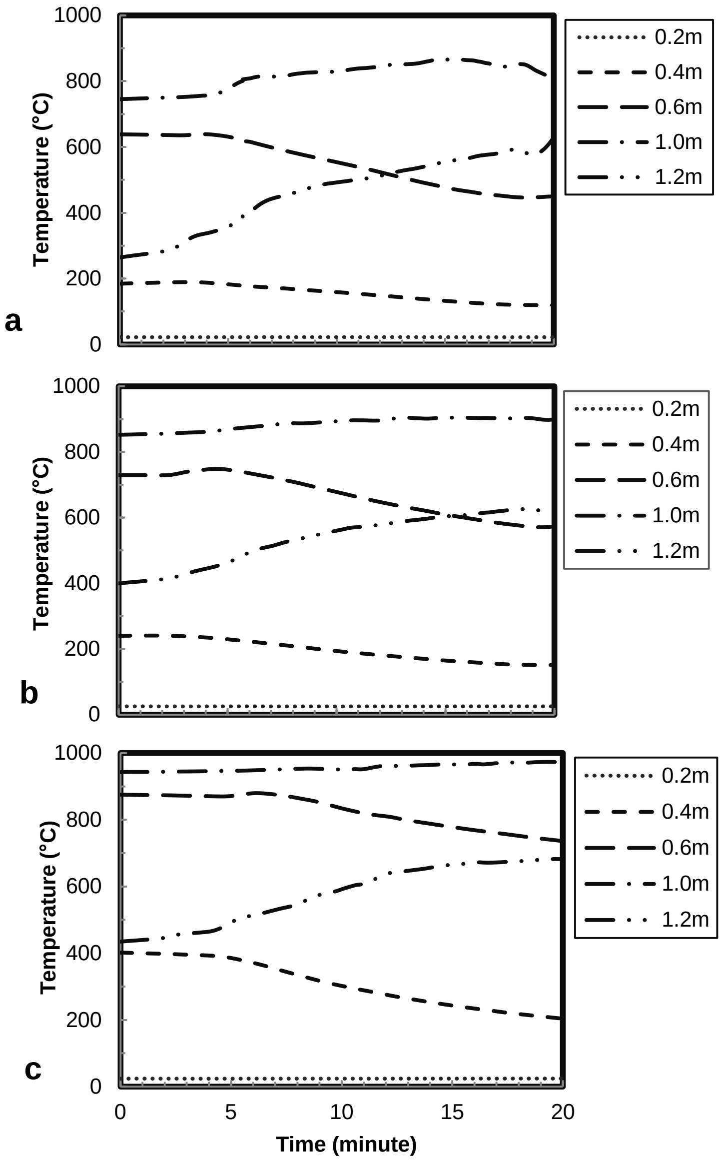

Fig. 2. Temperature profiles in auger gasification at (a) 760 °C, (b) 860 °C, and (c) 960 °C

Producer Gas and Condensables Yields

Figure 3 depicts the average concentration of CO, CO_2, and H_2 in the producer gas under the three temperature levels studied. The molar concentration of each of these gas species was determined using multi-gas analyzer (7905AQ model, NOVA Analytical Systems Inc.), which used a thermal conductivity detector for H_2 and infrared detectors for both CO and CO_2. The concentrations of both CO and H_2 increased with temperature from 12.8% and 4.7%, respectively, at 760 °C to 16.9% and 11.4%, respectively, at 960 °C. The CO_2 concentration, on the other hand, decreased with increasing reaction temperatures, from 14.0% at 760 °C to 11.6% at 960 °C. At atmospheric pressure, the volumetric energy density of H_2 and CO was 12.8 and 12.5 MJ m^{-3}, respectively. Accordingly, the higher heating value (HHV) of the producer gas, without considering the CH_4 content, varied from 2.20 MJ m^{-3} at 760 °C to 3.57 MJ m^{-3} at 960 °C. These CO, CO_2, and H_2 concentration trends were expected, based on the char gasification reactions, *i.e.*, the Boudouard and water-gas reactions. Both reactions are endothermic and yielded more CO and H_2 and less H_2O and CO_2 with the increase in temperatures.

$$C + CO_2 = 2\,CO\ (159.9\ \text{kJ mol}^{-1}) \qquad \text{[Boudouard reaction]}$$
$$C + H_2O\,(g) = CO + H_2\ (131.3\ \text{kJ mol}^{-1}) \qquad \text{[Water-gas reaction]}$$

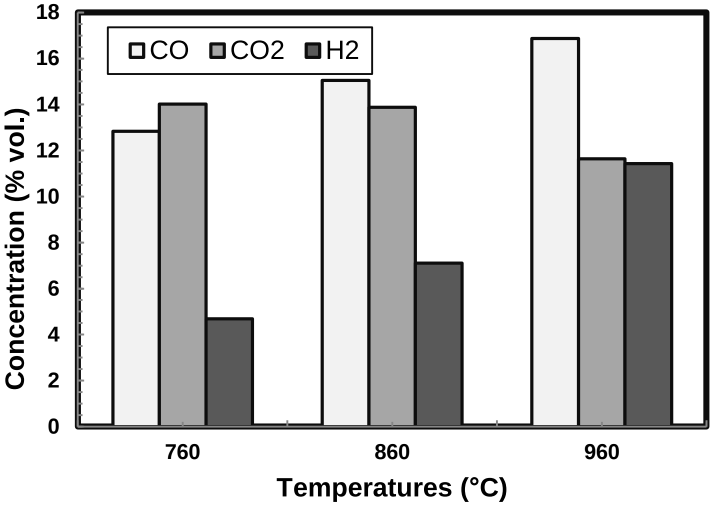

Fig. 3. Concentration of some product gases under different temperature levels

However, the concentrations of H_2 and CO, the energy-positive gas species, were still considerably low, *i.e.*, 10% and 16%, respectively, at the highest temperature. This result could be attributed to the low C and H concentrations in the starting material (Table 2), as well as the low heat transfer coefficient in indirectly-heated reactors (Brown and Brown 2012). It is worth noting that most studies that utilized auger reactors in biomass conversion have primarily used these devices for pyrolysis tests (Ingram *et al.* 2007; Pittman Jr. *et al.* 2012). In the context of gasification, however, increasing the biomass temperature and residence time could improve the conversion efficiency in auger reactors, thus maximizing H_2 and CO production.

The yield of producer gas varied within a relatively small range, from 0.59 m^3 to 0.80 m^3 per 1 kg of dry algae. These rates were significantly lower than those reported for traditional biomass such as pine wood sawdust, *i.e.*, more than 2.0 m^3 per 1 kg of dry, ash-free biomass (Narvaez *et al.* 1996). On the other hand, a study investigating the gasification of the microalga *Spirulina* to produce methanol reported that the gas yield ranges from 1.06 and 1.55 m^3 per 1 kg of algal biomass at temperatures between 850 °C and 1000 °C, respectively (Hirano *et al.* 1998). The low producer gas yield could be attributed to the high mineral content of algal biomass (greater than 40%). Using the dry, ash-free mass (DAF) as the basis, the producer gas yields in algae gasification tests became 1.02 to 1.38 m^3 kg^{-1} DAF. The difference between these dry, ash-free yields and those attributed to lignocellulosic biomass could be attributed to auger reactor performance.

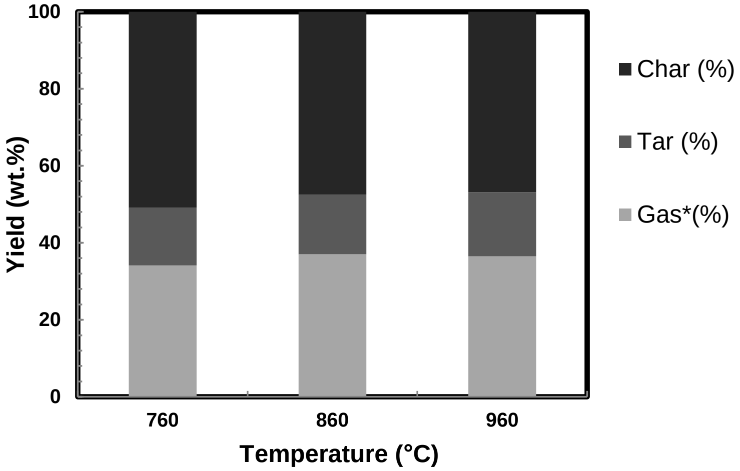

Fig. 4. Products distribution under different gasification temperatures

The high yield of condensables, 16.6% at 960 °C, further underlined the low gas conversion efficiency, even at such high temperatures (Fig. 4). In downdraft gasification, the yield of condensables (tar and water) has been shown to typically amount to less than 1% of the original fed biomass (Yamazaki *et al.* 2005). By contrast, countercurrent (updraft) gasifiers have been reported to yield condensables in amounts ranging from 12.7% to 37.2% of fed biomass; these numbers varied according to the type of feedstock and the operational parameters (Di Blasi *et al.* 1999). Earlier studies (Sadaka 2013; Sadaka *et al.* 2014), which utilized the auger gasification platform used in the current study, reported yields of condensables that varied from 18% to 34%. The auger gasifier, therefore, could be considered an intermediate platform between downdraft (concurrent) and updraft (countercurrent) gasifiers in terms of the yield of condensables.

Char Yields and Characteristics

Given the high ash content (minerals) of the algal biomass investigated, the char yields were around 50% of the algae fed into the system, as shown in Fig. 4. The decrease in char yields with increasing gasification temperatures, from 50.9% at 760 °C to 46.9% at 960 °C, could be explained by the increased reaction severity that favored heterogenous char reforming reactions (Huang *et al.* 2012) which facilitate carbon conversion. This increased carbon conversion translates to a decrease in the char yield and corresponding increases in yields of producer gas and condensables. Despite the high minerals content in the algal biomass and the high reaction temperatures used, no large aggregates were observed during or after the tests. Mechanical feeding (*via* a screw conveyor) might have been advantageous, in this case, in avoiding stagnant zones where hot spots typically occur and facilitate the formation of fused mineral aggregates (known as clinkers). The high concentration of silica (SiO_2) in the algae ash fraction, 71.8% (Table 2), could be attributed to the presence of diatoms, which utilize Si in building cellular walls and structures (Kroger *et al.* 2000).

Table 2. Characterization of Raw Algae and Product Chars

Temperature (°C)		**25**	**760**	**860**	**960**
Proximate analysis (%)					
	Moisture content (wb*****)	13.8	2.2	2.1	2.2
	Volatile matter (db******)	42.2	6.8	6.9	5.7
	Fixed carbon **†** (db)	15.9	18.1	12.6	12.6
	Ash content (db)	41.9	75.1	80.5	81.8
Ultimate analysis (%)					
	C	28.26	17.71	15.59	14.07
	H	3.63	0.58	0.41	0.70
	N	2.83	0.98	0.71	0.48
	O†	23.06	8.84	6.78	2.14
	S	0.57	0.64	0.66	0.74
Ash analysis (%)					
	Al_2O_3	3.55	3.33	3.38	3.36
	CaO	9.75	10.38	10.93	10.45
	Fe_2O_3	3.00	2.53	2.73	2.57
	MgO	1.20	1.22	1.21	1.20
	MnO	1.39	1.51	1.49	1.50
	P_2O_5	3.77	3.83	3.70	3.66
	K_2O	1.96	2.02	2.00	2.00
	SiO_2	71.8	72.30	70.76	71.54
	Na_2O	0.55	0.50	0.52	0.49
Higher heating value (MJ kg^{-1})		10.55	5.67	4.71	4.46
COD* (mg L^{-1})**		10,190	330	320	480

*****Wet, mass-basis
******Dry, mass-basis
† By difference
*******Chemical Oxygen Demand

The elemental analysis of the ash in the original biomass could assist in predicting the thermal behavior and sintering potential of the mineral oxides. The presence of alkali metals, such as sodium (Na) and potassium (K) influences the carbon conversion, as well as the yields of gaseous, liquid, and solid products. Chars and ash alkali minerals were shown to have a catalytic role, both as primary and secondary catalysts that reduce yields of tar and condensables (Sutton *et al*. 2001; Abu El-Rub *et al.* 2004; Lv *et al*. 2010). Yanik *et al.* (2013) reported a low bio-oil yields and high char yields during pyrolysis of macroalgal species, which was attributed to the presence of the alkali metals in the ash.

In addition to their catalytic role, ash metals are known to form low-melting temperature oxides that cause fusion and agglomeration during thermochemical conversion. The following indices (Mettanant *et al.* 2009) were devised to determine the sintering potential based on the higher heating value (HHV) of the feedstock and the relative amounts of sodium, potassium, and silica, as shown in Eq. 1.

$$\frac{(K_2O+Na_2O)}{SiO_2} > 1; and \ \frac{(K_2O+Na_2O)}{HHV} > 0.34 \qquad (1)$$

For the phycoremediation algae in this study, the values of both indices, 0.035 and 0.238, respectively, are below those associated with increased sintering tendency. This observation could help justify the use of this feedstock as an added fuel in co-firing of coal or lignocellulosic biomass without risking an increased sintering potential.

As shown in Table 2, the concentration of residual nitrogen (N) in the algae chars decreased progressively with the increase in reaction temperatures. Nitrogen loss during pyrolysis and gasification was attributed to thermal decomposition of N-rich components into NH_3, HCN, HNCO, during pyrolysis, and NH_3 and N_2 during gasification (Zhou *et al.* 2000; Di Nola *et al.* 2010). In a pyrolysis study of blue green algae and water hyacinth, the nitrogen loss was found to be predominantly in the form of NH_3, with lower concentrations of HCN (Yuan *et al.* 2011). They explained that the nitrogen in protein-rich feedstock, such as algal biomass, readily decomposes into NH_3. In this study, however, the concentration of nitrogen was not quantified in the product gas or in the condensate.

The elemental composition of the chars could be used to further understand the carbon conversion efficiency. The concentration of carbon progressively decreased from 28.3% in the raw algae to 17.7, 15.6, and 14.1% in the chars with increasing conversion temperature. Using the char yield in each test, the percentage of carbon retained in the biochar and that released in gas or liquid form could be computed using Eqs. 2 and 3, respectively.

$$Carbon\ retained\ in\ biochar\ (\%) = \frac{Char\ yield(\%) * Carbon\ Conc.\ in\ char\ (\%)}{Carbon\ Conc.\ in\ original\ feedstock\ (\%)} \quad (2)$$

$$Carbon\ released\ (\%) = 100 - Carbon\ retained\ in\ biochar\ (\%) \quad (3)$$

Using Eq. 2, the carbon retained in the biochar decreased with the increase in gasification temperature, from 31.9% of the original biomass carbon at 760 °C to 23.4% at 960 °C. This pattern was in agreement with the observed increases in gas yield upon increasing the conversion temperature. On the other hand, the carbon released (Eq. 3) was 68.1, 73.8, and 76.6% of the original carbon at gasification temperatures of 760, 860, and 960 °C, respectively. In gasification literature, the carbon conversion efficiency, which relates the amount of carbon released in the producer gas to that in the original biomass, typically fell between 70% and 90% (Worley and Yale 2012).

In the current study, if the condensables were re-injected into the gasification chamber and utilized to produce more energy-positive gases, the released carbon (%) could be considered a proxy for the carbon conversion efficiency. Despite the application of relatively high gasification temperatures, *i.e.*, 860 to 960 °C, carbon conversion in this study was still noticeably lower than the typical values reported in biomass gasification literature. Since the reaction severity is a function of both reaction temperature and time, it is clear the residence time was insufficient to facilitate complete conversion. The high yield of condensables and high C concentration in the char indicated that the residence times for both the solids and the devolatilized species were not sufficient. Either increasing the length of the heated reactor or reducing the rotational speed of the auger would increase the solids residence time and thus, the reaction severity. On the other hand, the volatile fraction (gas and condensables) needed a longer residence time at high temperatures to facilitate tar cracking and the water-gas reaction. Increasing the volatiles residence time could be accomplished as an added step, *e.g.*, by using a heated, coiled pipe that approximates the freeboard section in fluidized-bed gasifiers. Accordingly, the design of this added section (diameter, length, and temperature) could be informed by reported values of gas velocity and reactor height in fluidized-bed gasification studies.

TGA Characterization of Raw Algae and Biochar

Figure 5a shows the combustion weight-loss as a function of temperature for the raw algae, as well as the gasification chars produced under different temperatures. The weight-loss derivative curves (DTG), Fig. 5b, further elucidate the different combustion stages. In the raw algae, the weight loss proceeded in three consecutive stages: drying, devolatilization, and char oxidation.

The first stage, *i.e.*, drying, took place below 100 °C as the first weight-loss peak indicates (Fig. 5b). The volatile matter loss, the second stage, took place between 150 and 400 °C. The third stage, char oxidation, proceeded between 400 and 600 °C. These observations indicate that under extremely high heat transfer conditions, full conversion is achievable at or below a particle temperature of 600 °C.

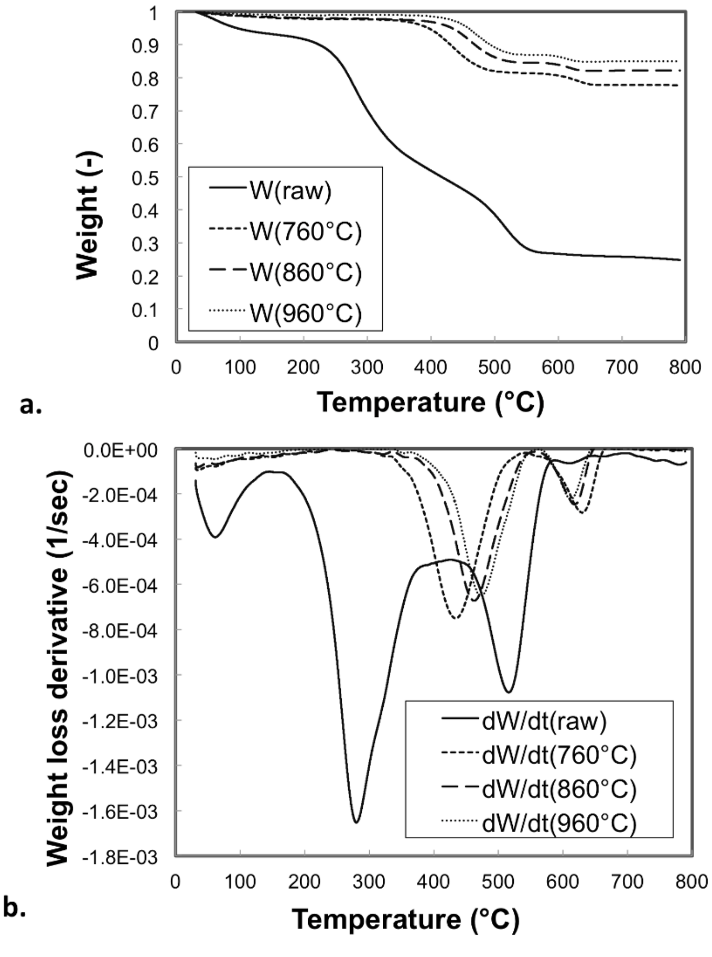

Fig. 5. Oxidation profile of raw algae and gasification chars at a heating rate of 5 °C min^{-1}: (a) weight loss profiles and (b) derivative of weight loss

For the gasification chars, no drying peaks were detectable. Similarly, no weight loss took place below 300 °C. This phenomenon could be attributed to the gasification weight loss, which involved the loss of moisture, as well as the devolatilization of the bulk of the volatile matter.

Two weight loss peaks were detected during the combustion of the algae chars. The temperatures corresponding to the decomposition peaks in each stage, as compared to those for raw algae, are listed in Table 3.

Table 3. Characteristics of Oxidation Thermogram for Raw and Charred Algal Biomass at a Heating Rate of 5 °C min^{-1}

Temperature (°C)	25	760	860	960
T_{p1} (°C)	279.8	433.5	462.1	472.8
$(dW/dt)_{p1}$ (mg s^{-1})	-1.65E-03	-7.50E-04	-6.72E-04	-6.52E-04
T_{p2} (°C)	515.7	629.5	617.8	611.6
$(dW/dt)_{p2}$ (mg s^{-1})	-1.08E-03	-2.83E-04	-2.46E-04	-2.22E-04

In the algae chars, the temperature corresponding to the first oxidation peak increased from 433.5 °C to 472.8 °C with the increase in gasification temperature from 760 to 960 °C. Earlier studies on the combustion of biomass pyrolysis chars reported peak decomposition to occur at 378 °C for olive kernels, 412 °C for cotton residue, and 509 °C for wood (Kastanaki and Vamvuka 2006). It is worth noting that, in the current study, the third decomposition stage, *i.e.*, char oxidation, for the raw algae took place at a higher temperature, 515.7 °C, than for the gasification chars. This observation could be attributed to the fact that under gasification, or any thermal treatment, the original biomass matrix is transformed into a new structure (biochar) that has its own thermal and oxidative properties. Keiluweit *et al*. (2010) demonstrated, on pine shavings, the consecutive stages of structural and compositional changes that take place with increasing the charring temperature from 100 to 700 °C. They indentified four distinct stages that are characterized by crystallinity and the aromaticity of the char matrix.

Implications of Results

With the proliferation of phycoremediation applications in industrial, agricultural, and municipal contexts, the yields of algal biomass harvests are expected to increase. Given their composition and unique biological structures, algal biomasses are not readily accessible for use in composting and anaerobic digestion. Similarly, thermochemical conversion of algal biomass faces various complications, mainly the high moisture and ash contents, and the low energy density. In addition to retrieving a fraction of the algae energy, however, thermochemical conversion processes could be thought of as a densification step for the algae minerals into a carbon-rich form (biochar). These biochars could be blended with lignocellulosic chars and applied to land, which would enhance the P content of the blend. Alternatively, these chars could be activated to produce a filtration medium. This alternative would work in tandem with the phycoremediation scrubbers to minimize further leaching and run-off of problematic minerals and metals.

CONCLUSIONS

1. The development of temperature profiles during auger gasification indicated the formation of different reaction zones, similar to those observed in fixed-bed systems.
2. Increasing the gasification temperature decreased the CO_2 yield but increased the yield of CO and H_2 and, consequently, the gas heating value.

3. Char yields decreased from 50% to 46% by increasing the gasification temperature from 760 °C to 960 °C.
4. The high ash concentrations in the raw algae biomass resulted in low gas yields and high char yields.
5. High condensables yields and high carbon concentrations in the char indicated low conversion efficiencies, even at the highest temperature tested.
6. The chars retained 27.8%, 21.2%, and 19.8% of the energy contained in a unit mass of raw algae at gasification temperatures of 760 °C, 860 °C, and 960 °C, respectively.
7. The carbon (C) concentrations in the algae chars were between 14.1% and 17.7%.
8. Concentration of phosphorous (P) and potassium (K) oxides in the char ash varied between 3.66% and 3.83%, and between 2.00% and 2.02%, respectively.
9. The TGA combustion analysis showed an influence of the gasification temperature on the char oxidation kinetics.

ACKNOWLEDGMENTS

The authors would like to acknowledge Dr. Marty Matlock, Dr. Thomas Costello and their team Morgan Welch and Heather Sandefur for contributing the algae feedstock. The authors also acknowledge the support of the Rice Research and Extension Center (RREC) in Stuttgart, AR. This manuscript is part of the USDA-NIFA project No. 2010-04269 titled "Integrated Resource Management Tools to Mitigate the Carbon Footprint of Swine Production in the U.S." The authors would like to thank the funding agency for their continued support. Preliminary results of this investigation were reported by the authors in a conference paper titled "Auger Reactor Gasification of Algal Blooms Produced in a Waste Water Treatment Facility," paper No. 12-1337915, presented at the 2012 ASABE Annual International Meeting in Dallas, Texas from July 29 to August 1, 2012.

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Article submitted: December 17, 2014; Peer review completed: February 10, 2015; Revised version received and accepted: March 3, 2015; Published: March 12, 2015.
DOI: 10.15376/biores.10.2.2609-2625