GASIFICATION AND PRODUCTION OF BIOCHAR FROM WASTEWATER GROWN ALGAE

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ABSTRACT

This paper presents the results of some preliminary experiments on gasification of algal biomass harvested from wastewater treatment HRAP, the production of biochar from pyrolysis and some beneficial properties of the resulting biochar. A laboratory-scale gasifier was constructed to mimic the conditions in a High Temperature Downdraft Gasifier (HTDG), HTDG requires a biomass with specific properties including: uniform size; structural integrity; low moisture content and; low nitrogen content to reduce NH_3 and NOx emissions. Since harvested algal biomass has a very high moisture content (typically ~96%) a drying step is required before gasification. Wastewater treatment HRAP algal biomass was able to be air-dried to 12% moisture in 24 hours during NZ summer conditions using a simple non-woven geotextile drying rack. Air-dried algal flakes were gasified in the updraft gasifier with 20.6% of the total energy content of the algae captured as water heating energy. Potential problems with nitrogenous gas emissions due to the high nitrogen content of algal biomass could be eleveated by using various adsorption and scrubbing technologies. Pyrolysis was used to produce a high quality biochar from air-dried algal flakes with a 28.1% conversion efficiency. For every kg of algal biomass that was converted into biochar, 0.44 kg of CO_2 was sequestered as biochar carbon. Pyrolysis of wastewater treatment HRAP algal biomass to biochar could sequester ~130 kg CO_2 per ML of wastewater treated in the HRAP. Powdered activated algal biochar had nitrate absorption capacity of 0.8 mg N/g which is similar to that found for other biochars e.g. wood. Powdered activated algal biochar had nitrate absorption capacity of only 0.8 mg N/g which is similar to that found for other biochars e.g. wood, but would be of little value for use in a final treatment polishing. A basic energy analysis indicates that there could be sufficient energy within algal biomass to dry freshly harvested algae for pyrolysis to sequester CO_2 as biochar.

KEYWORDS

Wastewater, CO_2, HRAP, Algae, Gasification, Pyrolysis, Biochar, Sequestration

1   INTRODUCTION

High rate algal ponds (HRAPs) are capable of recovering nutrient resources from wastewater as algal biomass that may be beneficially used as fertiliser and feed. Algal biomass may also be converted to biofuels through anaerobic digestion, transesterification, fermentation or thermal treatments such as super critical water, pyrolysis or gasification. Algal biofuel is a promising alternative to other biofuels as algae have much higher productivity and therefore require less land area than terrestrial crops. However, at current fossil fuel prices, the only economically viable method of algal production for biofuels is as a byproduct of wastewater treatment in HRAPs. This paper presents the results of some preliminary experiments on gasification of algal biomass harvested from wastewater treatment HRAP, production of a high quality biochar through pyrolysis and some beneficial properties of the resulting biochar.

1.1   GASIFICATION

Gasification is a process used to partially combust biomass in a high temperature (700-1000ºC), oxygen deficient enviroment to produce a high quality fuel gas (hydrogen and carbon monoxide) (Shetha et al. 2009) and biochar

(Lehmann et al. 2006). This fuel gas may be used to directly fuel a standard internal combustion engine. There are many different gasifier designs. The only gasifier that has proven to produce very low tar content gas is the commercially available High Temperature Downdraft Gasifier (HTDG). The HTDG is a continuous operation gasifier that can reach temperatures of 1500°C. The biomass moves slowly downwards in the HTDG and is converted into biochar as it goes through three main reaction zones (Figure 1):

(1) Pyrolysis zone, where the biomass is carbonised and releases a tarry fuel gas;

(2) Oxidation zone where air is injected to combust the tar and some of the biochar to carbon dioxide and water, and;

(3) The reduction zone where the lack of oxygen causes the biochar to reduce CO_2 and H_2O to CO and H_2
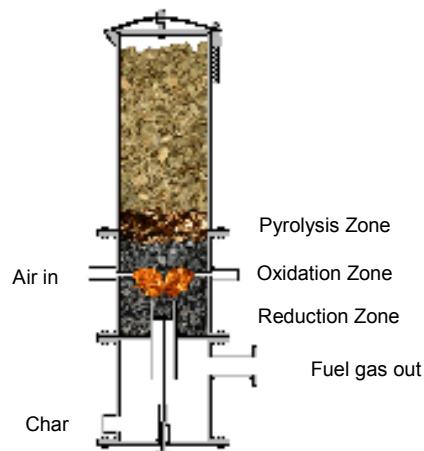

Figure 1:   Schematic Diagram of a HTDG

However, to operate effectively, the HTDG requires a biomass with specific properties including: uniform size; structural integrity (forms a biochar uniformly to avoid ash fusion which could potentially cause a blockage); low moisture content (as too much water will cool the oxidation zone and increase tar content in the fuel gas) and; low nitrogen content (to reduce nitrous oxide emissions). This has limited the use of HTDG gasification to high quality biomass such as wood (chips or blocks). The latter two properties are of particular significance to the gasification of wastewater treatment HRAP algal biomass, which has a high nitrogen content (typically 8% of dry weight) compared to other biomass, and has a very high moisture content (typically ~98%) when freshly harvested by gravity sedimentation. Therefore, a drying step is required before the algal biomass can be used for gasification.

1.1.1   NITROGEN EMISSIONS

An issue with the gasification and pyrolysis of algal biomass is that it has a high (~8%) nitrogen content most of which is converted into gaseous products (mainly ammonia and nitrogen gas with smaller amounts of NOx). For example, (Zhou et al. 2000) found that updraft gasification at 650 °C of peat (3% N) produced fuel gas containing 2100-2700 ppm ammonia; 100-600 ppm HCN and ~5 ppm of NOx.

1.2   BIOCHAR

Biochar is a charcoal that is formed by the incomplete combustion of biomass when burnt in an oxygen deficient environment (e.g. pyrolysis, gasification) (Gaunt et al., 2008). Biochar is a stable form of carbon which has been shown to be very resistant to degradation. Biochar is an excellent soil ammendment and has been shown to increase soil fertility (Mustafa et al. 2010) and as such has been used for thousands of years by Amazonian tribes to condition rain forest soils. Since biochar is not biodegradable it could be used as a means of sequestering atmospheric carbon into the soil for thousands of years (Lehmann et al. 2006).

Pyrolysis is the thermal decomposition of a material in an oxygen free environment. It produces a very tarry fuel gas that can be combusted for process heat or used as a bio-oil (Mohan et al. 2006). Pyrolysis is the typical method for the production of biochar. Previous research on gasification of algal biomass has been for the production of fuel gas (at high pressures with the aid of a catalyst) (Minowa et al. 1999); and for the production of bio-oil (Harino et al. 1998). There has been no previous research on the production of biochar from wastewater treatment algal biomass, however, biochar has been made from pyrolysis (at ~500-1000°C) of wastewater bacterial sludge (e.g. Mustafa et al., 2010; Kante et al. 2008) and algal biomass from pure cultures of several algal species (Grierson et al. 2009). The quality of biochar formed by HTDG is quite different to that formed by pyrolysis alone, as the tar is removed from the biochar at high temperature and the presence of oxygen in the oxidation zone and the biochar is then activated by reacting with carbon dioxide in the reduction zone lower down. The resulting biochar is more like activated carbon than charcoal (Dias et al. 2007). Activated carbon is a carbonized material that has been activated by either oxidation or reduction to open up the carbon structure. This activation increases the surface area of the carbon structure and causes it to become very effective at adsorbing chemicals from liquids and gases. In HTDG's, carbon dioxide gas causes the activation and the high temperature tempers the biochar to increase structural stability Some potential beneficial uses of activated biochar within wastewater treatment plants include: (1) adsorption of nitrate from wastewater (Mizuta et al., 2004) and; (2) removal of hydrogen sulphide from biogas which is adsorbed and oxidised (Kailiva et al. 1983; Bouzaza et al. 2003; Busca et al. 2003; Yonghou et al 2008; Kante et al. 2008; Pipatmanomai et al. 2009).

The aim of this study was to demonstrate that wastewater grown algal biomass can be gasified in a HTDG. The efficiency of pyrolysing algal biomass to produce biochar was also determined. The potential carbon sequestration by pyrolysis of algal biomass to biochar was estimated based on wastewater flow. Preliminary investigations of the beneficial use of activated biochar to adsorb nitrate from wastewaters were also conducted.

2   MATERIALS AND METHODS

2.1   PREPARATION OF ALGAL BIOMASS FOR GASIFICATION

Algal biomass was collected from the algal settling cones that harvest the algae from the effluent from pilot-scale wastewater treatment High Rate Algal Ponds at the Ruakura Research Centre, Hamilton, New Zealand (37°47'S, 175°19'E). The algal biomass was dried on the surface of drying racks made of a non-woven geotextile (Figure 2) in direct sunlight over several days during a New Zealand summer (Hamilton average summer temperature: 19 °C and; average humidity at 9 am: ~75%). The moisture content of the algal slurry and dried flakes was measured by drying a weighed sample in an oven at 80°C until constant weight was achieved (typically <24 hours).

Figure 1:   Drying algal biomass on non-woven geotextile drying rack

2.2   LABORATORY-SCALE GASIFICATION APPARATUS

This experiment was conducted to see if dried algal flakes could be gasified successfully using an HTDG. The oxidizing conditions and temperature of an HTDG were mimicked using a simple purpose designed laboratory-scale updraft gasifier stove that works like an HTDG but without a reduction zone. The laboratory-scale updraft gasifier stove was constructed from sheet metal and had a 5V fan to force air from the bottom up through the gasifier partially combusting the biomass into a gas that was then combusted in the air injected at the top of the stove. A similar updraft gasifier was designed by Reed et al. (2005). The updraft gasifier stove was run in two operational modes for the experiments: gasifying mode (to gasify algae); and pyrolysis mode (to provide heat from wood to convert algae to biochar) (Figure 3).
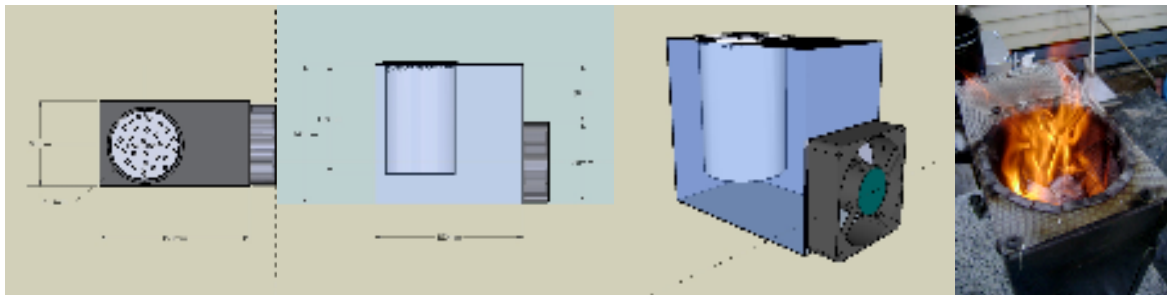

Figure 3:   Laboratory-scale updraft gasifier stove

2.2.1   GASIFICATION OF ALGAE

A 40 g sample of air dried algal biomass was weighed in an aluminium foil dish and then placed into the laboratory-scale updraft gasifier. The combustion was initiated with a small quantity (8 g) of kerosene. The fuel gas produced was burnt in the combustion zone of the laboratory-scale updraft gasifier which heated a 500 ml volume of water in a beaker that was placed on a stand above the combustion zone (Figure 4a). The temperature of the oxidation zone flame was recorded every 10 seconds for 5 minutes using a thermocouple (K-type,) placed 3 cm from the bottom of the gasifier. The temperature of the water was measured using a thermistor (LM335) and a simple datalogger. When the combustion was complete and the char had burnt to an ash, the reduction in water volume was measured. The total heat output was then calculated and compared to the total energy content of samples of the algal biomass measured in a bomb calorimeter (ISO Method 1928). This experiment was repeated three times. The third trial had residual heat in the reactor friom the previous trail.

2.2.2   PYROLYSIS OF ALGAE

The gasifier was then reconfigured to provide heat for pyrolysis of air dried algal flakes. A 20 g sample of algal biomass was weighed and placed in a 50 ml conical flask. The gasifier was fuelled with wood chips (Popular with a 10% moisture content). Once the wood chips were alight, the conical flask was placed on a stand over the combustion zone of the gasifier and heated (Figure 4b). The temperature within the flask was maintained above $600^{\circ}C$ (measured by a thermocouple (K-type) that was inserted into the flask). After ~1 minute the tarry gas from the heated algal flakes started to combust with flames appearing from the top of the flask. When the flames were no longer present it was assumed that the tar has been driven off. The flask was then taken off the stand and covered to prevent oxygen intrusion and reduce oxidation of the biochar. After cooling for 5 minutes, the remaining algal biochar was weighed and the conversion efficiency calculated. The experiment was repeated seven times.
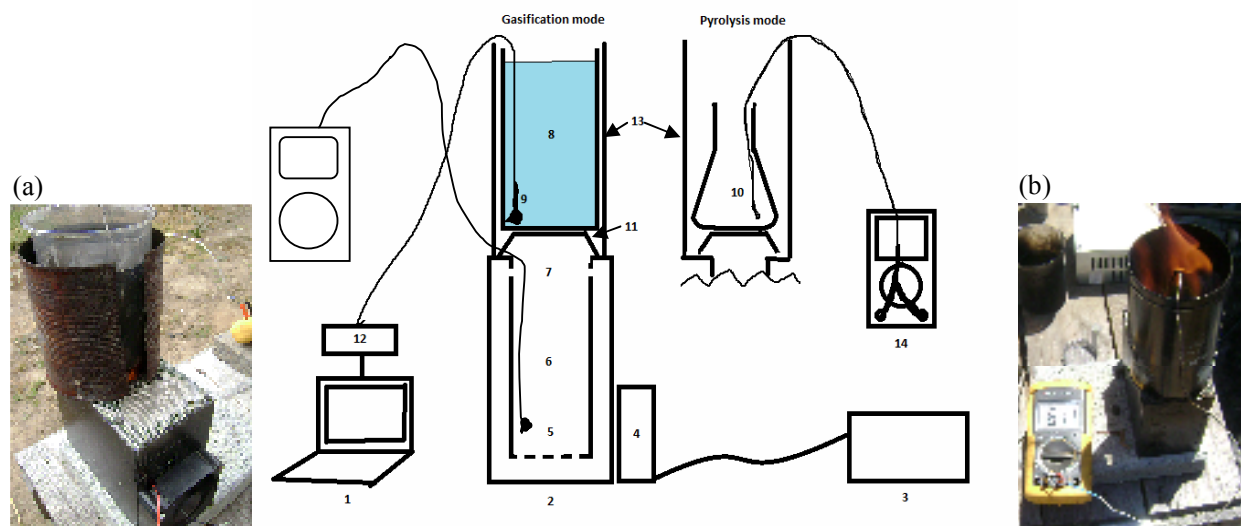

Figure 4:   *Laboratory-scale gasifier apparatus in (a) gasification mode and (b) pyrolysis mode: 1) computer and data acquisition; 2) gasifier chamber; 3) power supply; 4) small; (5V) fan; 5) oxidation zone; 6) pyrolysis zone; 7) combustion occurs; 8) 500 ml beaker containing water; 9) thermistor (LM335); 10) 50 ml conical flask; 11) stand; 12) PIC microcontroller; 13) metal shrouds; 14) thermocouple (K-type).*

2.2.3   PROXIMATE AND ULTIMATE ANALYSIS

Samples of algal biomass and algal biochar were sent to commercial laboratories: CRL Energy Ltd to measure: % moisture (ISO 11722); % ash (ISO 1171), % volatile solids (ISO 562), % fixed carbon (by difference); ash constituents (X-ray fluorescence analysis), and; University of Otago to measure: %CHN; %Oxygen (by difference),

2.2.4   NITRATE UPTAKE BY ACTIVATED BIOCHAR

Biochars of algae and wood prepared in the pyrolysis experiment were ground separately in a pestle and mortar. Two 1 g samples of both biochars and a 1 g sample of an activated carbon were weighed on foil trays and each placed into a test-tube. A 25 ml volume of ammonium nitrate solution (4.4 g N m^{-3} of nitrate) was added to each test-tube. After an hour the solution from each test-tube was filtered and the ammonium concentration was measured spectrophotometrically (Nessler's Reagent Method).

3 RESULTS AND DISCUSSION

3.1 PREPARATION OF ALGAL BIOMASS FOR GASIFICATION

Harvested algal biomass (98% moisture content) was air dried on a non-woven geotextile drying rack for one day during NZ summer conditions. The algal flakes (approximately 80 mm by 50 mm) easily peeled off the non-woven geotextile were then turned over and dried for a further day. Air drying reduced the moisture content of the algal flakes to ~12%. The algal flakes were found to be composed of layers with a large number of interstitial spaces (Figure 5); they were also difficult to break. These structural qualities (strong enough not to crumble, but loosely packed to enable gas circulation) could make air dried algal flakes an ideal biomass for gasification.

Figure 5:   Air-dried algal flakes

3.2 GASIFICATION OF ALGAE

The heat energy released from the burning fuel gas produced by the gasification of a 40 g sample of air-dried algal biomass to ash in the laboratory-scale updraft gasifier stove was calculated by measuring the change in temperature and volume (due to evaporation) of a 500 ml volume of water. The results of three replicate experiments are summarized in Table 1 with the total heat energy output of the algae calculated after subtracting the heat energy of the 8 g of kerosene (0.344 MJ; Bisio, 1995) used to initiate the combustion. The heat energy output measured in this study (4.58 – 4.93 MJ/kg) are at the high end of values measured for pure cultures of green algae (range: 1.4 to 4.8 MJ/kg) Grierson et al. (2009). The total energy content of samples of the algal biomass measured in a bomb calorimeter was found to be 23.06 MJ/Kg (Higher Heating Value, HHV), which is very similar to values previously reported for green algae (23.5 MJ/kg; ECN, 2010). The boiling efficiency was determined by dividing the measured heat energy by the HHV and then multiplying by 100.

Table 1:   Heat energy release from the gasification of air-dried algal flakes

Gasification experiment	1	2	3
Water loss from 500 ml volume (g)	6	8	12
Increase in water temperature (K)	81	81	81
% of algae remaining as ash	11.6	11.9	11.9
Heat energy output (J)	183,000	188,000	197,000
Heat energy output (MJ/kg)	4.575	4.700	4.925
Boiling efficiency (%)	19.9%	20.4%	21.4%

The average boiling efficiency (20.6%) of the updraft gasifier stove was similar to that found by Reed et al. (2005) and indicates that this simple apparatus was operating very efficiently. The consistency of gasification of the algal flakes is illustrated by the similar temperature profile of the oxidation zone in all 3 experiments (Figure 6). The slight difference in the profile of experiment 3 to that of experiments 1 and 2, was probably due to heat remaining in the system from the previous experiment, which was only conducted an 10 minutes earlier.
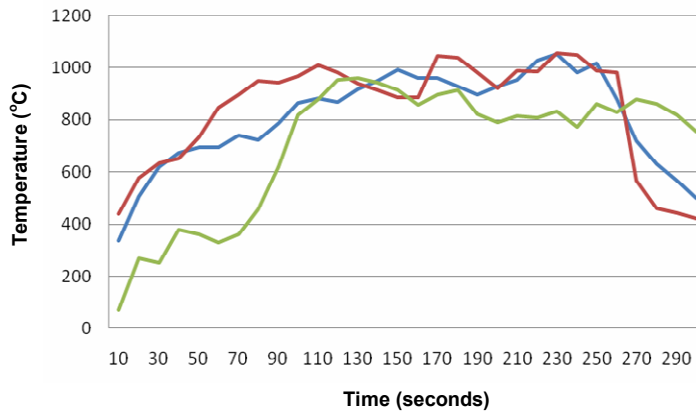
Figure 6:   *Algal gasification experiment oxidation zone flame temperature profiles*

3.3   PYROLYSIS OF ALGAE

The time taken for pyrolysis (at 600-650 ^oC) of 20 g of air dried algal flakes in a 50 ml conical flask until the tarry gas combustion flames were extinguished varied between 4.15 and 7.46 minutes in seven replicate experiments. However, the efficiency to conversion to biochar was very consistent, with an average of 28.1+/- 0.5%, which is lower than values measured for pure cultures of green algae (34 – 63%) Grierson et al. (2009). A comparison of the proximate analysis and HHV of algal flakes and algal biochar shows that the pyrolysis made a very high quiality biochar with very low volatile solids content (10.7%) and high fixed carbon content (Table 2) compared with typical pyrolysis biochar (Inguanzo et al., 2002). The HHV of the algal biochar was quite low compared with wood biochars. The ash content of the algal biochar was high compared with other algal biochars (< 10%; Hirano et al. 1998). This may be due the relatively high silica content (55% of the ash; Table 3) within the cell wall of Pediastrum (the dominant alga in the HRAP at the time of these experiments) compared with other green algae (Schwartz 1977).

Table 2:   *Proximate analysis and HHV of algal flakes and algal biochar formed by pyrolysis at >600 ^oC*

	Moisture Content (%)	Ash (%)	Volatile Solids (%)	Fixed Carbon (%)	HHV (MJ/kg)	Sulphur (%)
Algal flakes	6.9	11.3	71.3	10.5	23.06	1.1
Algal biochar	5.3	40.5	10.7	43.5	16.37	0.8

% are of sample as received

Table 3:   *Ash Consitituents by XRF of algae flakes*

SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	Na_2O (%)	K_2O (%)	TiO_2 (%)	Mn_3O_4 (%)	SO_3 (%)	P_2O_5 (%)
55.11	8.48	4.56	3.50	1.69	3.86	2.02	0.53	0.13	0.14	9.22

The heat released by the combustion of the tarry gas from the pyrolysis of 1 kg of algal biomass was found to be ~18,000 kJ. This heat energy is sufficent to raise the temperature of 7 kg water from 15 ^oC to 100 ^oC and then vapourise it and could reduce the moisture content of harvested algal biomass from 96% solids to 10% (suitable for pyrolysis). This calculation does not take into account the efficiencies of heat transfer or evapouration. There would appear to be sufficent energy within algal biomass to dry freshly harvested algae for pyrolysis to sequester CO_2 as biochar.

3.4   NITRATE UPTAKE BY ACTIVATED BIOCHAR

A comparison of nitrate uptake by powdered activated biochars of algae and wood with that of powdered activated carbon showed that the nitrate absorption capacity of activated biochars of algae (0.8 mg N/g) and wood (0.93 mg N/g) were similar, but were only half of that of activated carbon (1.95 mg N/g). The nitrate adsorption capacity of the biochars was similar to that (1.1 mg N/g) found for bamboo biochar (900 ^{o}C) (Mizuta et al. 2004). Although commercial activated carbon from the same study only had a nitrate adsorption capacity of 0.8 mg N/g. Park et al. (2003) found that activated carbon could adsorb ammonium from activated sludge effluent (1.1mg N/g of activated carbon). Assuming that ammonium adsorption onto biochar is half that for activated carbon, then the algal biochar could adsorb ~0.55 mg N/g. Assuming a HRAP algal concentration of 200 g algae m^{-3} wastewater and a biochar conversion efficiency of ~0.25 g char/g of algae, then 50 g biochar could be potentially produced per m^{-3} wastewater, which could adsorb 27 mg N per m^{-3} of ammonium in wastewater. This preliminary experiment indicates that biochar produced from wastewater treatment HRAP harvested algae would be of little value for use in a final treatment polishing.

3.5   MANAGEMENT OF NITROGEN IN PYROLYSIS

Pyrolysis of algal biomass (~6.2% nitrogen) to biochar (5.5% nitrogen) released ~47 g N / kg algae as gaseous nitrogen (mainly ammonia and nitrogen with a small amount of NOx). These nitrogenous gases need to be removed from the exhaust gas. NOx can be filtered out using a ferrous catalyst (Leppailahti et al. 1990). Lu (1996) found that pyrolysed (650°C) sewage sludge (19 % ash) activated with $ZnCl_2$ could be used to adsorb NOx (34.5mg of NO_2/g). Ammonia gas, however, has low adsorption to activated carbon or biochar (0.8-1.8 mg NH_3/g of activated carbon; Rodrigues et al. 2007), but could potentially be removed by water scrubbing (Melse and Ogink, 2005).

Interestingly, 25% of the mass of nitrogen in the algal biomass is stored in the biochar produced from that algae, but this nitrogen might not be available for plant growth because it has been incorporated into the carbon structure (Knicker, 2010).

3.6   CO$_2$ SEQUESTRATION POTENTIAL

The experiments conducted in this study indicate that it might be energetically feasible to use algal biomass harvested from wastewater treatment HRAP solely for biochar production to sequester atmospheric CO_2 and store it in a stable form in the soil. The energy produced by combustion of the algae would be used to dry the incoming harvested algal biomass, so there would be little net energy available for external use.

Analysis of the pyrolysis algal biochar showed that it had a carbon content of 43.5%. This sequestered carbon is very stable (as it withstood temperatures of 900°C under inert conditions) and is therefore assumed to indicate the amount of carbon that would potentially remain in the soil for thousands of years. Algal flakes were converted to biochar with an efficiency of 0.28 kg char/kg of algae, therefore 0.123 kg of carbon was sequestered as biochar per kg of algal biomass. Since, algal biomass typically assimilates 1.8 kg CO_2 / kg algae (assuming an algal carbon content of 46% dry weight) (Benemann 2003), 0.067 kg of carbon was sequestered as biochar per kg of CO_2 assimilated into algal biomass. In summary, 24% (0.44 kg) of the 1.8 kg of CO_2 assimilated into 1 kg algae could potentially be sequestered as biochar carbon. A typical wastewater treatment HRAP with average algal concentration of 300 g m^{-3}, could therefore sequester into biochar carbon ~130 kg CO_2 per ML of wastewater treated.

4   CONCLUSIONS

Wastewater treatment HRAP algal biomass was able to be air-dried to 12% moisture in 24 hours during NZ summer conditions using a simple non-woven geotextile drying rack.

Air-dried algal flakes were gasified in an updraft gasifier with 20.6% of the total energy content of the algae captured as water heating energy. However, due to the high nitrogen content of algal biomass it is recognised that there could be problems with high ammonia and nitrous oxide emissions from algal gasification.

Air-dried algal flakes were pyrolysed to a high quality biochar with a 28.1% conversion efficiency.
For every kg of algal biomass that was converted into biochar, 0.44 kg of CO_2 was sequestered as biochar carbon.

Pyrolysis of wastewater treatment HRAP algal biomass to biochar could sequester ~130 kg CO_2 per ML of wastewater treated in the HRAP.

Powdered activated algal biochar had nitrate absorption capacity of only 0.8 mg N/g which is similar to that found for other biochars e.g. wood, but would be of little value for use in a final treatment polishing

A basic energy analysis indicates that there could be suffcent energy within algal biomass to dry freshly harvested algae for pyrolysis to sequester CO_2 as biochar.

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