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Bio-char production from micro algal biomass of *Chlorella vulgaris*

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Abstract
In this study, biochar production was carried out using the dried algal biomass of *Chlorella vulgaris*. Algal biomass was subjected to pyrolysis process at various temperatures (such as 350, 400, 450, 500, 550, 600^{o} C) in pyrolysis chamber by slow pyrolysis method, biochar was obtained at range of 64 to 68% at 600^{o}C and also C: N ratio. In this study results showed the pyrolytic biochar has the potential to be used in agricultural plant production, as a fertilizer and soil conditioners. However, the nutrient contents in biochar and performance depend on the source of the feedstock, pyrolysis conditions and rate of application also has been investigated.
Keywords: biochar, pyrolysis, algal biomass, *Chlorella vulgaris.*

1. Introduction

Biochar is a form of charcoal produced from biomass, by a process known as pyrolysis. Pyrolysis means heating in the absence of oxygen, which prevents complete burning of the organic biomass (which happens in open fires) (Sohi *et al.,* 2009). It is rich in a stable form of carbon which is not oxidised by soil micro-organisms.

Biochar has unique properties that make it not only a valuable soil amendment to sustainably increase soil health and productivity, but also an appropriate tool for sequestering atmospheric carbon dioxide in soils for the long term in an attempt to mitigate global warming (Lehmann and Joseph 2009). Biochar application to soils is being considered as a means to sequester carbon (C) while concurrently improving soil functions (Verheijen *et al.,* 2010).

The term ‘Biochar’ is a relatively recent development, emerging in conjunction with soil management and C sequestration issues (Lehmann *et al.,* 2006). It has previously been used in connection with charcoal production (e.g., Karaosmanoglu *et al.,* 2000; Demirbas 2001). The rationale for avoiding the term ‘charcoal’ when discussing fuel may stem from the intent to distinguish it from coal.

Terra Preta ("black earth") was discovered by Dutch soil scientist Wim Sombroek in the 1950's, when he discovered pockets of rich, fertile soil in the Amazon rainforest (otherwise known for its poor, thin soils). Carbon dating has shown them to date back between 1,800 and 2,300 years (Glaser *et al.,* 2002).

Algal Biochar derived from the remediation of wastewater from aquaculture, agriculture, eutrophied natural waterways, or saline wastewater source could provide significant revenue stream in the future through energy co-generation, carbon credits from providing long-term soil carbon sequestration and sale as a soil ameliorant and fertilizer (Bird *et al*., 2011).

The feasibility of Biochar production from 3 kinds of freshwater algae, viz. Spirulina, Spirogyra and Cladophora was undertaken. Biochar could be generated at 550^{o}C under nitrogen atmosphere. The yields of Biochar were between 28-31% of the dry algae (Chaiwong, *et al*., 2012).

The algal Biochar represent a promising target for the generation of bioenergy through slow pyrolysis, leading to the production of freshwater and saltwater macro algal Biochars and their impact on plant growth. The production of Biochar from spirulina sp via the slow pyrolysis technique, spirulina sp performed at the temperature of 450 to 600^{o}C. The maximum yield of Biochar occurred at approximately 500 and 550^{o}C (Chaiwong *et al*., 2013).

Biochar properties

Biochar is best described as a ‘soil conditioner’. Despite many different materials having been proposed as biomass feedstock for Biochar (including wood, crop residues and manures), the suitability of each feedstock for such an application is dependent on a number of chemical, physical, environmental, as well as economic and logistical factors (Verheijen *et al.,*2010).

This paper focuses on production of biochar from CHN and S, P, K, Ca and Mg at the pyrolysis temperature range between 350, 400, 450, 500, 550, 600^{o} C which follows semi indirect heating method. The properties of both the raw biomass and biochar such as physico-chemical, nutrient and other important properties were studied, analyzed and compared for carbon sequestration potential in the atmosphere to mitigate greenhouse emissions.

2. Materials and methods

We have chosen *Chlorella vulgaris* as a culture for the carbon sequestration studies, which is collected from the research laboratory of Phycospectrum Environmental Research Centre (PERC), Chennai, Tamilnadu, India. CFTRI used as a culture medium for outdoor cultivation. Improvised CFTRI medium was used for cultivating micro algae outdoors and the composition is as follows (Venkataraman, 1985).

Biochar Production

The preliminary trials were conducted with laboratory scale pyrolysis set up fabricated for the production of biochar from the dried algal biomass of *Chlorella vulgaris*. Before charring, the air dried algal biomass was sieved (<0.25mm) in crucibles sealed with lids to prevent from the oxygen entering, and pyrolysis in a muffle furnace. In the muffle furnace, an empty metal drum was perforated on the sides (about 5mm) and an opening measuring 30cm in diameter was created on top of the container to facilitate the arrangement of fuel wood for burning. The bottom of the drum was completely removed. Fire was set in the container to facilitate charring. In the course of burning, rice husk was heaped on the sides of the drum container that had the fuel wood burning. Heat passed through the perforated holes and charred the algal biomass into carbonated algal biomass.

The algal biomass were slowly pyrolyzed in the pyrolysis unit between temperature rate of 350^oC, 400^oC, 450^oC, 500^oC, 550^oC, and 600^oC by using semi-indirect heating method, in each temperature 500g of dried algal biomass was filled in the container and allow it for charring for 1hour. The biochar were cooled, collected and then grounded down to about <0.25mm sieved and stored in a refrigerator (at 4^oC) before use.

Characteristics of the Biochar were examined as follows; Concentration of elemental C, H, N, S, P, K, Ca and Mg at Indian Institute of Technology Madras (IIT Madras).

Carbon and nitrogen analysis

The analysis method is based on the complete and instantaneous oxidation of the sample by "flash combustion" which converts all organic and inorganic substances into combustion products. The resulting combustion gases pass through a reduction furnace and are swept into the chromatographic column by the carrier gas which is helium. The gases are separated in the column and detected by the thermal conductivity detector which gives an output signal proportional to the concentration of the individual components of the mixture. The results are comparable to those obtained by traditional methods. The sample to be analyzed is weighed into a tin container and loaded into the auto sampler. The sample is then deposited into the combustion reactor which is maintained at 1020^oC.

The sample and container melt and the tin promote a violent reaction in a temporarily enriched atmosphere of oxygen. Under these conditions even thermally resistant substances are completely oxidized. The mixture of combustion products pass first through an oxidation catalyst of chromium trioxide in the reaction/combustion tube. The combustion products, those of interest being CO_2, N_2 and NO_x, along with some water, then pass through a second tube known as the reduction reactor. It contains metallic copper kept at 65^oC. The excess of oxygen is removed and at this temperature the nitrogen oxides are reduced to elemental nitrogen, which together with CO_2 and water pass to the magnesium perchlorate tube which removes the water.

The helium stream then flows through a chromatographic column separating the nitrogen and carbon. From there the gases flow through the thermal conductivity detector which generates an electrical signal proportional to the concentrations. Analysing a standard of known composition under the same conditions makes it possible to calibrate the instrument and quantify the content of nitrogen and carbon.

Microwave digestion for S, P, K, Ca and Mg analysis in ICP-OES

A known weight of the sample was digested with 3 ml of Nitric acid in CEM microwave digester using MARSX press (self-regulating microwave vessel) under the following conditions.

Stage	Maximum power	% power	Ramp (min)	Pressure (psi)	Temperature º C	Hold (min)
1	1600 W	75	10: 00	-	200	15:00

The digested solution was made up to 25 ml using de-ionized water and it was thoroughly filtered using Whatmann 40 filter paper and the clear solution was analyzed by ICP-OES and the following results were obtained. A blank solution was also prepared in a similar manner and the intensity values were subtracted.

The percentage weight can be calculated from the equation:

$$\text{Wt \%} = \frac{\text{Ppm (mg/L) x Volume in ml x dilution factor x } 10^{-4}}{\text{Weight of Sample in grams}}$$

3. Results and discussion

We have chosen *Chlorella vulgaris* as a culture for the carbon sequestration studies, which is collected from the research laboratory of Phycospectrum Environmental Research Centre (PERC), Chennai, Tamilnadu, India. CFTRI used as a culture medium for outdoor cultivation. The experiment studies have chosen for the production of biomass. *Chlorella vulgaris* was inoculated into open raceway pond containing 1000litre tap water along with modified CFTRI medium.

The algae was harvested by settling method, during the process algal cells allowed to dense and settled in bottom of the raceway pond. For dry weight analysis, the algal cultures were pelleted. Then, cells were washed with glass distilled water again and again, dried it in hot air oven for 24 hours or until constant weight. Dried algal biomass used for biochar feedstock.

Algal Biochar production

A sample of 500g of dried algal biomass of *Chlorella vulgaris* was subjected to pyrolysis in various temperatures such as 350, 400, 450, 500, 550, 600^{o}C for time period of one hour inside the muffle furnace. Carbon, Hydrogen, Nitrogen and micronutrients were analysed, the results were presented in Table 1 and Figures 2 and 3.

Chaiwong, *et al*., 2012 was studied in deferent algal species to produce biochar by slow pyrolysis and they obtained the yields of Biochar were between 28-31% of the dry algae, from the results of our experiment biochar percentage was high between 64 to 68% when 550 to 600^{o}C (Table 1 and Figure 1) using feedstock of *Chlorella vulgaris* and Carbon, hydrogen and nitrogen percentage was high when algal biomass was subjected to pyrolysis at 600^{o}C.

Therefore, the hydrogen content of the microalgae samples tested in this study was assumed to be in a similar range, i.e., approximately 7%wt. It is known that the carbon content of the biomass correlates proportionally to the heating value of the biofuel, while the oxygen content affects the heating value in an inverse manner.

High oxygen content is not a desired property for high energy density biofuels. Results from this study showed that green microalgae contain higher carbon content. Therefore, green microalgae are assumed to be better candidates for biofuel production in terms of energy content. Meanwhile, low nitrogen and low sulphur content in microalgal biomass are highly desirable for making environmental friendly biofuels.

Table.1. Analysis of Algal Biochar

S No	Temperature	Percentage(%) of biochar	Carbon %	Hydrogen %	Nitrogen %	Sulfur %	P %	K %	Ca %	Mg %
1	350^{o}C	57.4	8.62	0.16	0.58	0.41	3.16	0.49	0.194	2.43
2	400^{o}C	52.4	7.11	0.02	0.42	0.30	4.70	0.55	12.63	1.92
3	450^{o}C	62	8.12	0.02	0.52	0.26	3.72	0.61	11.57	2.00
4	500^{o}C	56	15.4	0.12	1.12	0.27	3.42	0.52	12.11	1.90
5	550^{o}C	64	16.16	0.16	1.72	0.46	1.38	0.37	9.58	1.71
6	600^{o}C	68	**16.41**	**0.36**	**2.3**	0.26	3.31	0.47	9.79	2.04

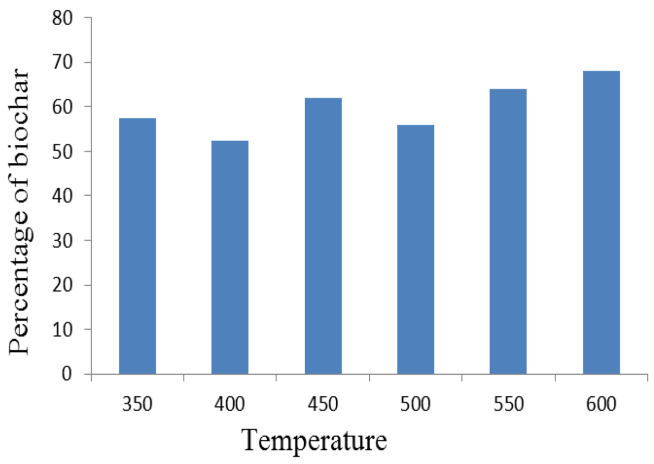

Figure.1. percentage of algal biochar

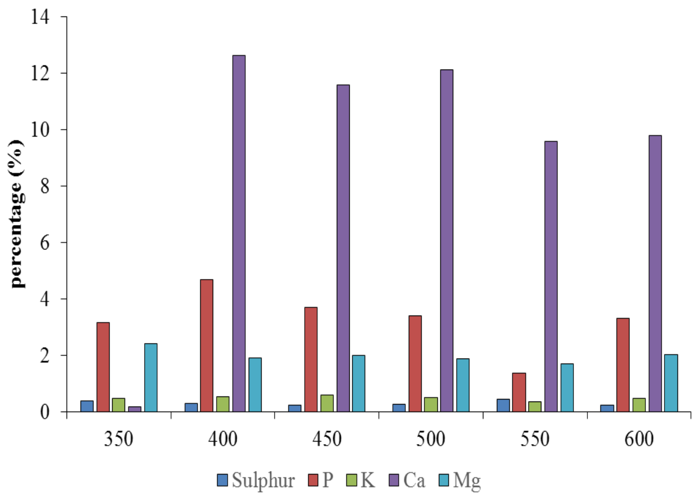

Figure.2. Analysis of micro nutrients in algal biochar

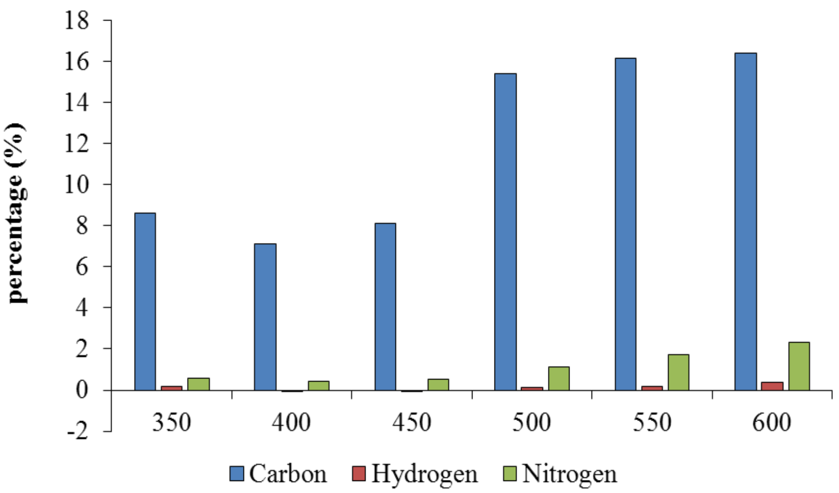

Figure.3. Analysis of macro nutrients in algal biochar

Results showed that the microalgal biomass samples tested in this study all contain very high levels of nitrogen and sulphur. Thus, processing of the microalgal biomass would require additional treatments to remove the undesirable heterogeneous elements in order to meet the biofuel specifications. Ash is a by-product of most biomass thermal conversion processes, including pyrolysis and gasification. Ash content would very likely affect the process design and operation, as well as the product purification processes and product quality. Examining individual minerals in the microalgal biomass also provides valuable information for the microalgae cultivation from the aspect of nutrient requirements

4. Conclusion

Based on the above discussion it is clear that biochar prepared at higher temperature contains a higher proportion of the stable organic matter than that of lower temperatures. The stable organic matter yield index increased up to 450 to 600°C. This temperature pyrolysis is much applicable for using biochar for soil carbon sequestration. The temperatures of pyrolysis condition viz 450 to 600°C are good enough for the preparation of biochar for the biomass of *Chlorella vulgaris.*

The study showed that pyrolytic biochar has the potential to be used in agricultural production. However, the nutrient contents in biochar and performance depend on the source of the feedstock, pyrolysis conditions and rate of application. For further experimental studies carbon and hydrogen rich Biochar was used for soil applications.

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