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Full Paper

Biochar production from freshwater algae by slow pyrolysis

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Abstract: A study on the feasibility of biochar production from 3 kinds of freshwater algae, viz. Spirulina, Spirogyra and Cladophora, was undertaken. Using a slow pyrolysis process in a specially designed reactor, biochar could be generated at 550^{o}C under nitrogen atmosphere. The yields of biochar were between 28-31% of the dry algae.

Keywords: biochar, slow pyrolysis, carbon-negative technology, algae, Spirulina, Spirogyra, Cladophora

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INTRODUCTION

Biochar technology is promoted as a carbon-negative technology [1]. Showing high potential as a solid biofuel, biochar can also be used for carbon sequestration and for improving soil conditions [2]. Biochar is a stable form of carbon [1-7], being more stable than the organic form and capable of remaining in the soil for hundreds or thousands of years [1-2]. This means that biochar can perform an important role in helping to sequester carbon from the atmosphere [6-8]. A considerable reduction in nitrous oxide (N_2O) emissions from biochar-amended soils have also shown [1-2]. N_2O is a greenhouse gas 300 times more potent than CO_2 and it is mainly associated with the use of nitrogen fertilisers [9]. Being highly porous, the biochar structure also helps improve soil conditions and water retention capability of the soil as well as increase its nutrients and surface area [10].

Biochar is produced from a thermochemical process in which biological materials (wood and wood waste, energy crops, aquatic plants and their waste by-products) are heated under a condition of limited or no oxygen [8]. The thermochemical conversion can be categorised into

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gasification, pyrolysis and liquefaction [11]. The pyrolysis process is usually used for biochar production because the technique is relatively simple and inexpensive and allows considerable flexibility in both the type and quality of the biomass feedstock [12]. Pyrolysis can produce the biofuel as gas, bio-oil and biochar. The proportion of the products is dependent on the process, which can be divided into 3 subclasses: slow pyrolysis, fast pyrolysis and intermediate pyrolysis [13], depending on the operating conditions. The proportions of the produced forms of fuel from wood are shown in Table 1 [14]. The slow pyrolysis, which gives a maximum yield of biochar, has been widely used for decades in charcoal kilns where the combustion occurs in the absence of oxygen. A slow heating rate is maintained up to 400-700°C [15]. At this low temperature range, a high carbon recovery from the organic biomass is obtained in the pyrolised biochar. For a higher temperature range of 700-800°C, the cation exchange capacity of biochar itself can also be improved, but a lower carbon yield (about 5% loss) is obtained. The optimum biochar production temperature in terms of carbon is recommended at 500°C [16].

Table 1. Mean composition of post-pyrolysis feedstock (wood) residues from different pyrolytic conditions [14]

Process	Liquid (bio-oil)	Solid (biochar)	Gas (syngas)
Fast Pyrolysis Moderate temperature (~500 °C), short hot-vapour residence time (<2s)	75% (25% water)	12%	13%
Intermediate Pyrolysis Low-moderate temperature, moderate hot-vapour residence time	50% (50% water)	25%	25%
Slow Pyrolysis Low-moderate temperature, long residence time	30% (70% water)	35%	35%

Algae have been promoted as a source of energy due to their advantages such as their fast growth rate, which is 10-340 times that of oil crops, and their less requirement of cultivation area. Besides, algae cultivation can be carried out not only in natural waters, i.e. sea water and freshwater, but also under such poor condition as in wastewater. This means that the algae can produce bio-energy without competition with the food production sector for cultivation space [17]. The energy conversion from algae can be carried out by 2 processes [18]. One is the biochemical conversion by which biofuel in the forms of biodiesel or ethanol such as that from marine green alga *Chlorococcum littorale* by dark fermentation [19] can be produced. For biodiesel, a specific type of algae, such as *Botryococcus braunii* or *Chlorella* spp., which give a high oil content of 30-75% wt of dry algae is normally required [20]. The second process is the thermochemical conversion that changes all types of algae into energy products via heat reaction; biochar is a by-product from this process. Algal biochar has a lower carbon content, surface area and cation exchange capacity compared with the lignocellulose biochar but has a higher pH and gives a higher content of nitrogen, ash and inorganic elements (P, K, Ca and Mg). The algal biochar could therefore be utilised to reduce the acidity of the soil and increase its inorganic nutrients [21]. However, only a few studies have been reported on biochar production from algae.

In this paper, a study on algal biochar production from three types of freshwater algae, viz. Spirulina (*Spirulina* spp.), Spirogyra (*Spirogyra* spp.) and Cladophora (*Cladophora* spp.), was carried out by slow pyrolysis technique. These algae, compared to other algae types used for biodiesel production [18], have a low oil content.

MATERIALS AND METHODS

Algae and Preliminary Analysis

Three studied samples of dry freshwater algae, viz. Spirulina (*Spirulina* spp.), Spirogyra (*Spirogyra* spp.) and Cladophora (*Cladophora* spp.), were of commercial grade (Figure 1). The first one is the micro-type and the other two are the macro-type. Spirulina is a genus of cyanobacteria and the dried samples are available in the local market. Spirogyra (locally known as Tao) and Cladophora (locally known as Kai) are common filamentous green algae [22] which can be found and collected from Nan River in the northern part of Thailand.

Before pyrolysis, each algal sample was characterised using ultimate analysis and proximate analysis. The former was performed as described by Channiwala and Parikh [23] while the latter was performed as described by Parikha et al [24].

Figure 1. Samples of dry algae: (a) Spirulina; (*b*) Cladophora; (c) Spirogyra

Thermo-Decomposition of Algae

Thermo-decomposition of organic matter under pyrolysis can be characterised by thermogravimetric analysis (TGA), in which the amount and rate of change in the weight of material due to decomposition, oxidation or dehydration is measured as a function of temperature in the form of a TG curve. Its derivative with respect to temperature is a DTG curve. The temperature at the peak (minimum or maximum) of the DTG curve shows the activation of the thermochemical reaction. If the peak of the DTG curve occurs at a low temperature, the reaction can be easily performed while the height of the curve corresponds to the capability to release volatile matter during the volatilisation reaction.

In this study, the tested algae were fed into a thermogravimetric analyser (PerkinElmer TGA7) and the tested conditions were controlled under nitrogen atmosphere. The heating program was: 50-135^{o}C (10^{o}/min.); constant at a 135^{o}C (5 min.); 135-900^{o}C (100^{o}/min). After that, the temperature was kept constant under oxygen atmosphere for 15 min. The TG and DTG plots could then be performed from the experimental data.

Fixed-Bed Pyrolysis

A 125-g sample of each dried alga was fed into a stainless steel fixed-bed reactor (21 cm high and 6 cm in diameter). The experimental set-up is shown in Figure 2. Nitrogen gas was fed at a flow rate of 30 ml/min. for 30 min. to remove air in the reactor before heating. The reactor was heated up at a rate of 8^{o}C/min. until the temperature reached a set temperature of 550^{o}C, at which it was then kept constant for 60 min. The gas leaving the reactor was condensed in two water-cooled condensers and the liquid (bio-oil) was stored in two collection flasks while the solid residue (biochar) remained in the reactor. Each experiment was performed in triplicate and the results averaged. After pyrolysis, the biochar products were subjected to ultimate and proximate analyses in the same manner as the dry algae before pyrolysis.

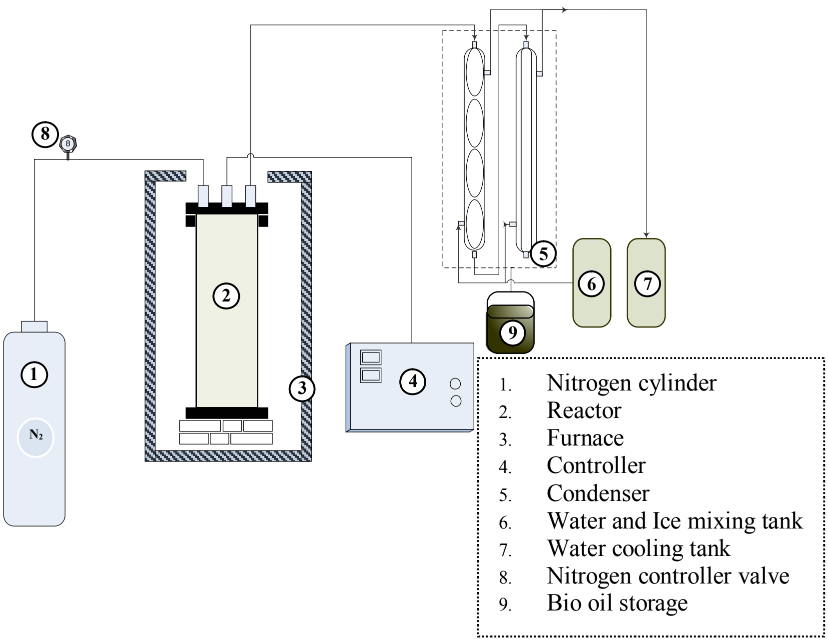

Figure 2. A schematic sketch of the pyrolysis experimental set-up

RESULTS AND DISCUSSION

The results of ultimate and proximate analyses of the dried algae are shown in Table 2. While Spirogyra and Cladophora are macrophytic green algae and Spirulina is a microphytic blue-green algae, the composition characteristics of Spirulina are quite similar to those of Spirogyra. For instance, both have a high carbon content and HHV, which should make them particularly suitable as raw material for generating biochar.

The pyrolytic characteristics of the three algae at temperature between 50-900^{o}C as determined by TGA are shown in Figure 3. The percentage of the existing weight as function of temperature (TG curve) showed that there were three stages occurring during the pyrolysis process. The first stage (up to about 200^{o}C) was dehydration; the weight loss was due to moisture removal

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from the sample. The next stage (200-600°C) was devolatilisation; the weight loss in this stage was about 60% due to the loss of volatile components. The last stage (600-900°C) was solid decomposition; at this stage the weight loss was slower. The DTG plots of the tested algae are also shown in Figure 3. In the devolatilisaton stage between 200-600°C, the peak in the DTG plot for Spirulina was highest compared with Spyrogra and Cladophora, which means that highest volatile matter was released resulting in highest yield of bio-oil.

Table 2. Results of ultimate and proximate analyses of dried algae

Analysis	Algae		
	Spirogyra	Cladophora	Spirulina
Ultimate Analysis (%)			
Sulfur	0.57	5.29	0.49
Carbon	39.26	28.78	42.83
Hydrogen	6.11	4.02	6.02
Nitrogen	6.65	3.06	4.09
Oxygen*	47.41	58.85	46.57
Proximate Analysis (%)			
Moisture	8.45	5.00	8.04
Ash	13.99	33.42	6.98
Volatiles	65.48	60.61	68.15
Fixed Carbon	12.08	0.98	16.83
HHV (MJ/kg) **	22.34	16.22	23.42

* By difference; ** Higher heating value, estimated by correlation of Channiwala and Parikh [23]

Normally, organic material is mainly composed of cellulose, hemicelluloses, lignin and extractive matter. Due to a lower cellulose and hemicellulose content and higher extractive matter content in algae compared with other kinds of biomass, a lower pyrolysis reaction temperature of the former can be expected. Table 3 compares the decomposition of algae and some other kinds of biomass. The temperatures at which the highest amount of volatiles in the biomass could be expelled out (temperatures at maximum decomposition rate) are given. It can be seen that the temperatures for the algae were around 300-330°C, which were lower than those for other forms of biomass. Thus, the pyrolysis reaction of the algae could occur more easily and with lower energy input. The maximum decomposition rate was also lower, which indicates that the amounts of volatile matter from the algae or the yields of bio-oil were lower. On the other hand, the amounts of solid residue from algae (biochar and ashes) at the end of the pyrolysis were observed to be higher than those from other forms of biomass.

The products and their distribution resulting from the slow pyrolysis of the three algae in the specially designed reactor are given in Figure 4 and Table 4 respectively, from which it can be

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observed that the bio-oil yield from Spirulina was highest and that from Cladophora was lowest. The biochar yields from all algae samples were somewhat similar, viz. 28-31% by weight of the dry algae.

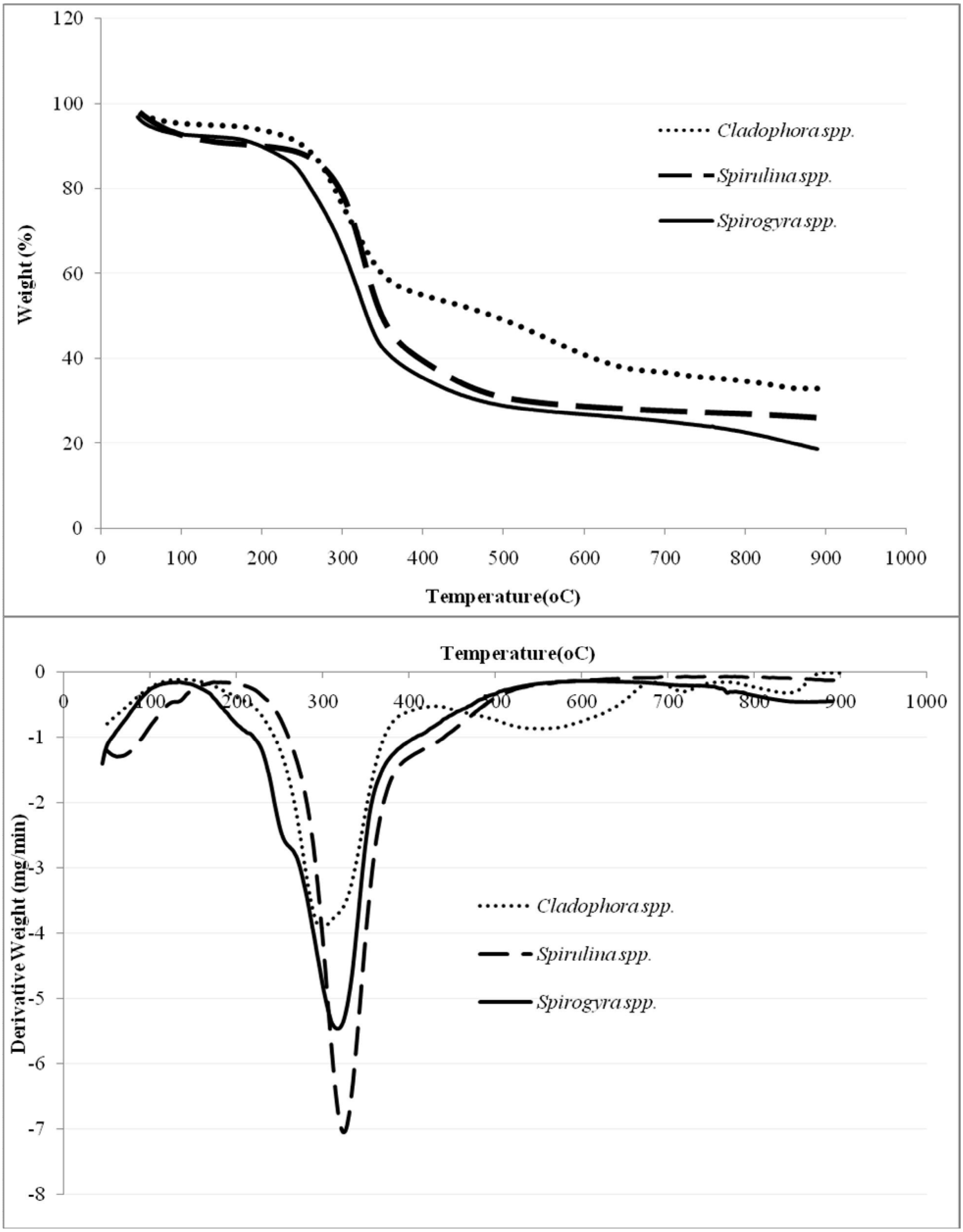

Figure 3. TG (top) and DTG (bottom) plots for tested algae

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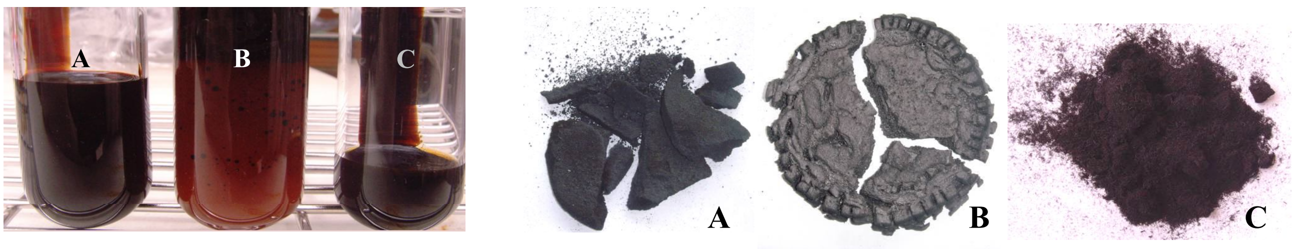
Table 3. Comparison of decomposition of algae and other forms of biomass [25]

Biomass	Temperature at maximum decomposition rate (°C)	Maximum decomposition rate (% min^{-1})**	% Solid residue at 900°C
Corncob	346	27.9	10.00
Rice husk	367	31.0	12.60
Eucalyptus	361	31.0	13.30
Sawdust	367	18.6	13.60
Palm shell	377	17.9	20.80
Coconut shell	355	18.2	22.07
Spirulina*	324	7.04	25.96
Spirogyra*	318	5.49	18.61
Cladophora*	300	3.92	32.21

* Results from present work
** Value of maximum decomposition rate is the percentage of maximum weight loss rate from DTG compared with initial weight.



(a) **(b)**

Figure 4. Bio-oil and biochar from slow pyrolysis of algae (A: Spirogyra, B: Spirulina, C: Cladophora)

Table 4. Product distribution from pyrolysis of algae at 550°C

Product	Product distribution (%wt)		
	Spirulina	Spirogyra	Cladophora
Gas*	23	29	30
Liquid (bio-oil)	46	43	39
Solid residue (biochar)	31	28	31

* By difference

The results of proximate and ultimate analyses of algal biochar products and other solid fuels are shown in Table 5. A high-quality solid fuel should have a high amount of fixed carbon with low volatile components and ash content or its chemical components should consist of a high carbon and hydrogen content in order to give a high heating value [26]. As shown in Table 5, peat (S-H3), German Braunkohle lignite and charcoal represent solid fossil fuels from low to high quality. Biochar from Spirulina and Spirogyra have the fixed carbon content similar to that of German Braunkohle lignite while their volatile components are lower. Spirogyra biochar also has the carbon content close to that of German Braunkohle lignite, although its hydrogen content is lower and nitrogen content higher. Thus, biochar from Spirulina and Spirogyra has high potential, after ash removal, to be used as fuel.

Table 5. Results of proximate and ultimate analyses of algal biochar compared with other solid fuels

Name	Fixed carbon %	Volatiles %	Ash %	HHV (MJ/kg)	C %	H %	O %	N %	S %	Ref.
Peat (S-H3)	26.87	70.13	3.00	22.00	54.81	5.38	35.81	0.89	0.11	[26]
German Braunkohle lignite	46.03	49.47	4.50	25.10	63.89	4.97	24.54	0.57	0.48	[24]
Charcoal	89.10	9.88	1.02	34.39	92.04	2.45	2.96	0.53	1.00	[24]
Oak char	59.30	25.80	14.90	24.80	67.70	2.40	14.40	0.40	0.20	[24]
Cladophora coelothrix char	-	-	32.10	-	34.60	1.50	-	3.30	-	[21]
Cladophora patentiramea char	-	-	47.00	-	20.30	1.20	-	1.70	-	[21]
Spirulina char	44.55	7.63	47.82	15.78	45.26	1.24	0.28	2.57	0.07	*
Cladophora char	26.68	35.50	37.81	16.68	51.14	0.56	0.69	1.98	1.86	*
Spirogyra char	59.66	16.81	23.53	22.96	62.37	0.37	4.07	2.11	0.48	*

* Results from present work

Lehmann et al. [8] suggested that the efficiency of carbon sequestration by algal bio-char is obtained when the carbon conversion into biochar leads to a sequestration of about 50% of the initial carbon. In this study, as seen from Table 5, the biochar from Spirogyra seems to be the most suitable candidate for carbon sequestration. The carbon content of Spirogyra char is also close to that of oak char and higher than that of the recently studied green tide algae (*Cladophora coelothrix* and *C. patentiramea* [21]). The high ash and nitrogen content in the algal biochar can also be beneficial to agricultural soil, especially acidic or nutrient-defficient soil [10].

CONCLUSIONS

This study has demonstrated an algal biochar production process by slow pyrolysis for three types of freshwater algae, namely Spirulina, Spirogyra and Cladophora. The quality of the biochar obtained was comparable to that of certain established solid fuels as well as biochar obtained from other forms of biomass. However, the temperature used for production appeared to be lower.

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