Renewable Energy 131 (2019) 617–624

Contents lists available at ScienceDirect

Renewable Energy

journal homepage: www.elsevier.com/locate/renene

# Elemental, morphological and thermal analysis of mixed microalgae species from drain water

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ARTICLE INFO

*Article history:*
Received 3 February 2018
Received in revised form
14 July 2018
Accepted 18 July 2018
Available online 19 July 2018

*Keywords:*
Bioenergy
Microalgae-coal blend
SEM-EDX
*Stigonematales* sp.
Thermogravimetric analysis

ABSTRACT

In this study, *Stigonematales* sp. microalgae were collected from drain water and characterized for its' morphological edifice, elemental composition, thermal condition and energy generation capacity by using scanning electron microscopy, energy dispersive X-ray, thermogravimetric analyzer and bomb calorimeter, respectively. Scanning electron micrographs revealed the top view of microalgae and ash pellet with carbon coated specimens at low voltage (5.0 kV) through the secondary electron image detector. Elemental analysis revealed all the major and minor constituents of this microalgae species and its' ash in terms of dry weight (%) and atomic weight (%). Thermogravimetric analysis was conducted at heating rate, 10 °C/min and this experimental results determined moisture content, volatile matter, ash content and fixed carbon of the sample with 4.5%, 35%, 39.5% and 21%, respectively. Microalgae powder blended with bituminous coal by 75%, 50% and 25% measured calorific value 14.07 MJ/kg, 19.88 MJ/kg and 26.42 MJ/kg, respectively. Microalgae (75%) -coal (25%) blend showed excellent amount of energy content, 24.59 MJ/kg. Microalgae blended with coal unveiled an outstanding outcome with elevation of the volatile matter and drop of the ash content. Optimization of microalgae-coal blend in large-scale application can initiate bright future in renewable energy exploration.



## 1. Introduction

Energy is essential in sustaining the quality of life for all beings, especially to humans. Energy from fossil fuels such as gas, coal and petroleum has been exploited for decades. Since the worlds' energy crisis in 1970s, energy sustainability has become very important in order to secure the economic growth. However, oil still remains as the dominant fuel in the world's primary energy consumption which is about 33.6% of the global total share in the last years [1–3]. Due to this reason, researchers are trying to find an optimal use of renewable energy such as hydro, solar, wind, wave, geothermal and bioenergy [4–7,9–11].

Microalgae are considered as one of the most efficient bioenergy sources like other energy producing terrestrial crops [12–14]. Microalgae conduct photosynthesis process by converting solar energy and $CO_2$ into $O_2$ and complex structured energy content which can be extracted as either liquid fuel like bioethanol, biodiesel and others or solid fuel like microalgae pellets as supplement for coal and mixture with other energy biomass to generate heat and electricity [15–17]. From the last decade, microalgae has been hailed as a versatile bioenergy source prior to producing an enormous array of value added products, oil enrichment up to 80%, prudent usage in diverse aspects, $CO_2$ recycles and waste uptake in heavy metal waste producing industries [18,19]. Besides energy production, microalgae is known as a natural wastewater purifier by utilizing water pollutants such as nitrogen, phosphorus and other heavy materials as well as balancing eco-system in water [19,21,22]. The dominant bioenergy producing microalgae groups are Chlorophyceae, Chrysophyceae, Cyanophyceae and Bacillariophyceae [23]. Microalgae maintain simple biological structure, they are presumed one of the most primitive microorganisms, usually do not interrupt human and animal food-chain, grow exponentially by 3.5 h in every type of water like freshwater, saltwater and wastewater and lead to 30–100 times higher energy per hectare compared to any terrestrial plants [24].

The energy content of microalgae biomass is formulated by the

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https://doi.org/10.1016/j.renene.2018.07.082
0960-1481/

presence of carbon (C), oxygen (O), hydrogen (H), Nitrogen (N) and other elements [24]. C and O weight as well as O/C ratio usually play the most significant role to determine heating value (energy per unit mass), energy content, combustibility and moisture content of the biomass as well as possibility of blending with other biomass type. The higher O/C ratio indicates the lower energy content of biomass [25–27]. As a result, elemental analysis of biomass is being considered one of the most effective characterizations for any kind of possible energy generation from biomass including microalgae [24]. Energy-Dispersive X-Ray (EDX) and Scanning Electron Microscopy (SEM) is usually implemented to estimate elemental, chemical and physical properties of biomass, biochar and ash quantitatively as well as comprehensive morphological illustration [28]. Garrate-Reed and Bell defined EDX analysis as highly effective technique for determining the elemental constituents of a sample and can be used to derive chemical concentrations with reasonable accuracy, especially if there is standard available [29]. Besides SEM-EDX, wavelength dispersive X-Ray analysis, electron energy-loss spectroscopy, auger electron spectroscopy, X-ray photoelectron spectroscopy, X-ray fluorescence, atom probe, XRD, Raman spectroscopy, FTIR spectroscopy are being applied for chemical, elemental and microanalysis [28,29]. For thermal treatment, thermogravimetric analysis (TGA) is popularly performed for miscellaneous biomass combustion from ambient temperature to very high temperature with 600°C–950 °C range to monitor the different stages of moisture removal, de-volatilization and ash content by high temperature furnace [27,30].

The main objectives of this study were: (i) To conduct morphological analysis of microalgae pellet by scanning electron microscopy (SEM), (ii) To perform quantitative elemental analysis of microalgae, microalgae ash and bituminous coal by energy dispersive X-ray (EDX), (iii) To apply two different pelletizing techniques: hand-pelletizer and hydraulic press, (iv) To determine the thermal conditions by thermogravimetric (TGA) analysis with 24°C–850 °C temperature and (v) To blend microalgae powder with bituminous coal powder with three different ratio (25%, 50% and 75%) for identifying the escalating rate of calorific value and volatile matter.

## 2. Materials and methods

### 2.1. Net calorific value (NCV)/higher heating value (HHV) analysis of microalgae with different ratio of coal

*Stigonematales* sp. mixed microalgae were collected from rainwater drains of Universiti Brunei Darussalam and then they were sun-dried 2 weeks in the open air; later, dried biomass was crushed into fine powder and preserved in air-tight jar in room temperature. The preserved microalgae powder was sieved with micro-sieve to remove the large particles as well as impurities. Measurement range of micro-sieve was 45–50 μm (diameter), laboratory test mesh sieve. 1 g of fine microalgae powder was pressed into pellet in two different techniques: hand pelletizer (C-200 by P.A. Hilton, United Kingdom) performed with anti-clockwise mechanical force by human and hydraulic press with 4 tons pressure (Model: PE/B/79 TONS-ON-RAM manufactured by International Crystal Laboratories, USA) by standard ASTM D 4703 method [31]. Each pellet's net calorific value or higher heating value was characterized according to standard ASTM E711-87 (2004) [25,32] by the Digital Bomb Calorimeter, C-200 by P.A. Hilton (United Kingdom) at the Biomass and Fuel Cell Laboratory of Department of Chemical and Process Engineering, Universiti Brunei Darussalam. The pellet was placed into the bomb calorimeter, the bomb was pressured with 25 psi pure oxygen ($O_2$), then pellets were combusted and calorific value of pellets for both approaches was recorded. After combustion, ash content was determined according to the ASTM D 3174 standard method [33].

Bituminous coal was collected from Indonesian local market and applied for microalgae-coal blend for this experiment. The coal was crushed into fine powder by a mortar and pestle, then sieved with micro-sieve and blended with microalgae powder in 3 different percentages as 25%, 50% and 75% separately. 1 g of each type of microalgae-coal blend was pelletized by hydraulic press with 4 ton pressure.1 drop of deco flux (binder) was added for each pellet for well-binding and higher stability. Hydraulic press was used to make these pellets in order to stabilize the pellet, remove all the porosity and maintain the same pressure for all the pellets of different ratio of microalgae-coal mixture. All pellets were combusted by bomb calorimeter and calorific value for each pellet was determined. Calorific value of the experimented (100%) bituminous coal was also characterized with the similar procedure.

### 2.2. Pellet density(PD), energy density(ED) and lower heating value (LHV)/net calorific value (NCV) calculation

Pellet density was calculated by the mass and volume of the pellet (Eq. (1). The mass of pellet was determined by the analytical balance and volume was measured by multiplication of pellet height, width and depth while they were measured by the digital vernier calliper in the laboratory. Pellet density (PD), energy density (ED), volatile matter (VM) and hydrogen content (H) were determined followed by Eqs. (1) and (2) [34] and Eq. (3) [35], respectively.

$$PD = \frac{m}{V} \tag{1}$$

Where, m = mass of sample (kg) and V = volume of sample ($m^3$)

$$ED = NCV \times PD \tag{2}$$

Where, ED = Energy density ($MJ/m^3$), NCV= Net calorific value (MJ/kg), PD= Pellet density ($kg/m^3$)

$$LHV = HHV - 2.454(MC\% + 9H) \tag{3}$$

where, 2.454 = Enthalpy difference between water vapour and liquid water in biomass per MJ/kg at 25 °C.

### 2.3. Morphological and elemental analysis by scanning electron microscopy (SEM)-energy dispersive X-ray (EDX) analysis of microalgae

This study has performed morphological analysis of *Stigonematales* sp. pellet by SEM-EDX. Microalgae pellets were carbon-coated to increase the conductivity in order to penetrate the pellet and the inner structure of pellet was snapped by Schottky Field Emission Scanning Electron Microscope, JSM-7610F (Japan Electron Optics Laboratory Co. Ltd., Japan) in the Geology SEM Laboratory in Faculty of Science, Universiti Brunei Darussalam. With the same SEM-EDX machine, the pellet samples were attached onto the EDX sample holder and placed carefully on analyzing chamber where the pressure was auto-controlled by the machine. For EDX, samples were not carbon-coated to determine the genuine elemental composition. After 10–15 min of process initiation, the machine determined the weight (%) and atomic weight (%) of the pellet elements. The EDX analyzer determined both weight and atomic weight of all elements over 100% in total. The elemental analysis of microalgae pellets, microalgae ash pellets and coal were experimented.

### 2.4. Thermogravimetric analysis

Thermogravimetric analysis of *Stigonematales* sp. microalgae sample was conducted according to standard ASTM E1131, ISO 11358 [36]. Approximately 61.5 g of microalgae powder in a very small ceramic crucible was measured by micro-balance pan. The crucible with sample was set in the thermogravimetric analyzer Setaram TG-DTA/DSC (SETARAM Instrumentation, France) in Physics Laboratory in Faculty of Science, Universiti Brunei Darussalam. The experiment was conducted at 10 °C heating rate under inert, Argon (Ar) gas and oxidative ($O_2$) gas flow rate, 60 ml/min providing the appropriate environment for the test. Gas environment was pre-selected as thermal-oxidative combination for the TG analyzer: air/oxygen ($O_2$) for oxidative decomposition and argon (Ar) gas for thermal decomposition. The furnace temperature was set from ambient temperature at 24 °C–900 °C. The initial sample weight was set as 100%. The weight and temperature detail were monitored by using a TGA program SETSOFT 2000. The whole combustion process consumed 2 h 10 min and at 850 °C, the combustion process stopped automatically. Then TG analyzer plotted percent weight loss curve versus temperature what determined the mass losses of all stages of combustion from initial stage till end of combustion. From that, we determined the sample mass loss in each stage of combustion and made ratio of sample mass of different stages with total sample mass (original sample mass) and moisture content (MC), volatile matter (VM) and ash content (AC) were calculated over 100%. In brief, the total MC%, VM% and AC% were determined from the mass vs. temperature curve and fixed carbon (FC%) was calculated by Eq. (4) [37].

$$FC\% = 100 - (MC\% + VM\% + AC\%) \quad (4)$$

## 3. Results and discussion

### 3.1. Bioenergy analysis

Table 1 delineated two different approaches of pelletizing methods by hand pelletizer and hydraulic press in terms of pellet density, NCV, GCV, energy density, H content and AC%. The pressure inserted on hand-pelletizer was human-hand force driven and not precise where with a hydraulic press, pressure was mechanically commanded with 4 tons. Pellet composed by hydraulic press was almost impenetrable and pellet density was 0.61 g/cm$^3$ higher than hand-pelletizer approach. Sample pellet by hand-pelletizer exhibited quite higher calorific value and lower ash content compared to hydraulic press approach probably due to better combustion quality. To note, pelletizing approaches were performed in different periods, thus moisture content and impurities of the sample could be lightly varied as well as decoflux (binder) was used for pellets through hydraulic press whereas hand pelletizer did not require any pellet binder. NCV and GCV also diverged for separate approach and impacted on energy density. Energy density played a significant role to optimize the transportation logistics. This parameter estimated the bioenergy storage per unit area and ventured the desired densification technique for energy storage, dust reduction and minimization of transportation cost [38]. Pellets by hydraulic press escorted energy density 4.12 GJ/m$^3$ premier than pellets by pelletizer what summed up the cost optimization by the hydraulic press approach. According to the energy logistics study of A.K. Kurchania [39], if energy density of any biomass feedstock can be obtained 8–9 GJ/m$^3$ more than usual energy density of it, transportation cost can be saved up to 40%–50%. Table 1 depicted both these two techniques.

To bind the pellets well, decoflux (binder) was applied during hydraulic press usage, though no binder has been used for pelletizer. The binder may add some subsidiary charge, though other biobinder e.g. potato starch, corn starch can be deployed [19]. Due to porosity, hand-pelletizer pellets held higher H content than hydraulic press pellet. However, pellets by hydraulic press were much well-constructed and dust-free rather than pellets prepared by hand pelletizer. That led to the conclusion, pelletizing by hydraulic press can maintain specific pressure for all pellets and form stable, dust-free pellet shape compared to hand-pelletizer. For any further characterization of microalgae or other biomass, hydraulic press pelletizing approach is recommended over hand-pelletizer for pellet homogeneity and more accurate measurement and analysis for energy and elemental composition.

The microalgae fine powder was blended with bituminous coal powder with 3 different ratios to identify the possibility of using microalgae for co-firing with coal. Table 2 illustrated the microalgae-coal blend and pure coal characterization result. Table 2 demonstrated that increased coal content minimized pellet density and fouling (ash) albeit calorific value and volatile matter of microalgae were elevated simultaneously. While pure *Stigonematales* sp. contained net calorific value 7.9–8.6 MJ/kg, after mixing with bituminous coal (25%) the net CV inflated approximately 6 MJ/kg more which meant 15% elevation of CV and ash reduced 15.38% where in previous study, *Chlorella* sp. mentioned only 2.33% less ash and 1.235 MJ/kg CV improvement with similar blending ratio [23]. Pellets for coal-microalgae combination were prepared by hydraulic press to assess the precise pressure, avoid dust, mass loss and revamp pellet solidity. Table 2 also depicted that the bituminous coal for the mixture in this study contained net CV 29.78 MJ/kg and AC 11.25%, which can be considered as an ideal fuel to generate adequate heat [26,27]. With 50% coal blend with the microalgae sample, 35.41% ash has been diminished as well as 11.9 MJ/kg CV was upgraded where other microalgae species like *Chlorella* strains ameliorated only 4.585 MJ/kg CV and 8.2% ash in previous experiments. Therefore, the coal mixed with microalgae manifested positive impact on CV improvement and slugging reduction. Finally, 25% microalgae with 75% coal boosted the calorific value very high, 26.42 MJ/kg. According to the study of [40], ash content of bituminous and lignite coal for coal industry can be obtained maximum 39.25% and 39.78%, respectively. So, microalgae powder blended with coal (Microalgae: Coal-50:50 and

**Table 1**
Bioenergy values of microalgae pellet with different pelletizing technique.

| Pure Microalgae Pellet (100%) | Mass of pellet(g) | Volume of pellet (cm$^3$) | Pellet Density (g/cm$^3$) | Net Calorific Value (MJ/kg) | Gross Calorific Value (MJ/kg) | Hydrogen (H) content (%) | Energy Density (GJ/m$^3$) | Ash Content (%) |
|---|---|---|---|---|---|---|---|---|
| Hand-Pelletizer Approach | 0.676 | 0.57 (L × W × H: 1.00 cm × 1.00 cm × 0.57 cm) | 1.18 | 8.57 | 9.94 | 3.15 | 10.16 | 36.71 |
| Hydraulic Press Approach (pressure: 4 Ton) | 0.5 | 0.279 (L × W × H:1.00 cm × 1.306 cm × 0.214 cm) | 1.79 | 7.98 | 8.81 | 2.94 | 14.28 | 59.1 |

**Table 2**
Bio-energy properties of microalgae blended with coal.

| Sample items | Mass of pellet (g) | Volume of pellet ($cm^3$) | Pellet Density ($g/cm^3$) | Calorific Value (MJ/kg) | Energy Density ($GJ/m^3$) | Ash Content (%) |
|---|---|---|---|---|---|---|
| Microalgae (75%) + coal powder (25%) | 0.5 | 0.373 (L × W × H:1.00 cm × 1.324 cm × 0.282 cm) | 1.34 | 14.07 | 18.85 | 43.72 |
| Microalgae (50%) + coal powder (50%) | 0.51 | 0.4 (L × W × H:1.00 cm × 1.318 cm × 0.304 cm) | 1.29 | 19.88 | 25.78 | 23.69 |
| Microalgae (25%) + coal powder (75%) | 0.35 | 0.311 (L × W × H:1.00 cm × 1.318 cm × 0.236 cm) | 1.12 | 26.42 | 29.73 | 14.24 |
| Pure coal sample (100%) | 0.2 | 0.2794 (L × W × H:1.00 cm × 1.306 cm × 0.214 cm) | 0.71 | 29.78 | 21.31 | 11.25 |

25:75) can be projected to be used in coal industry for heat and energy production as fuel supplement albeit pure *Stigonematales* sp. microalgae is not recommended for pure combustion for heat production purpose due to higher amount of ash.

With the improvement of coal mixture, pellet density has been diminished since microalgae sample was fluffy where coal powder was heavy with immense energy content. Microalgae in different ratios with coal boosted the energy density with 1.25–12.13 $GJ/m^3$ which can be a significant parameter to minimize the transportation and storage cost of raw material. *Stigonematales* sp.-bituminous coal blend unveiled an outstanding outcome for adequate heat generation and optimized calorific value and volatile matter for both coal and microalgae. The scaled-up application of this blend may open a new window to green energy mercenary in the fuel market.

### 3.2. Morphological analysis

The microalgae pellet was experimented through LM and SEM and for this morphological analysis, pellets were prepared by hand-pelletizer. Fig. 1(a) illustrated the surface view of microalgae pellet with light microscopy and the view displayed some pores, small dust particles on the top due to the light crack on the pellet top. Owing to uncertain pressure and lack of precise control, small cracks usually take place around the pellet. LM did not require a vacuum environment and presented the porosity. However, with LM, the resolution was not high and it described only the surface view, thus the figure could not elaborate the pellet view comprehensively. In Fig. 1(b), SEM identified the pellet from top and side view with low-porous, congested and densely solid form; particles were very strenuously shaped what demonstrated the homogeneity, intact and contamination-free sample. Fig. 1(c) and (d) manifested the consistency of non-porosity behaviour of the pellet. Moreover, SEM maintained high vacuum environment and consumed 15–20 min to drop internal pressure at 3 Pa for retaining a vacuum atmosphere what indicated enough permeability through microalgae pellet. Based on Fig. 1, SEM provided very high quality, exquisite, substantial, inclusive and well-contrasted view of pellet prior to the low accelerating voltage (5.0 kV), short working distance (7.3mm-7.4 mm) and secondary electron image detector [41,42].

### 3.3. Elemental analysis

Performing electron excited X-ray microanalysis with energy dispersive X-ray through scanning electron microscopy is being deemed as one of the most core, meticulous and authentic techniques to characterize the microstructure of any organic or inorganic material [43]. SEM-EDX analysis for this study was performed with an entirely vacuum environment and the experimental results yielded quantitative elemental analysis with all superior (C, O, N, Ca) and inferior constituents (Fe, S, Al, Si, W, Ni) of microalgae pellet, ash pellet and coal excluding gaseous elements (Table 4 and Table 5).

#### 3.3.1. Organic elements of biomass and ash

Table 3 represented C, O and O/C of several popular biomass on dry weight (%) basis and Table 4 presented elemental analysis of microalgae and microalgae ash (dry basis) by SEM-EDX. Organic elements for *Stigonematales* sp. and ash (dry basis) were mainly C, O and N. According to Table 4, C, O and N for dried microalgae pellets and ash were 30.30%, 40.87%, 6.36% and 21.54%, 40.15%, 1.75%, respectively. The C amount of the experimented biomass sample was less than other energy generating terrestrial crops (45.10%–52.1%) and agricultural residues (41.4%–49.4%) where O content was in the similar range of other biomass (Table 3). The higher proportion of O compared to C will cause the lower heating energy for this species since C–C bonds (heat source) will be lower than O–C bond [26]. Based on the study of Chaula et al. [27], ratios of atomic oxygen to carbon (O/C) and atomic hydrogen to carbon (H/

**Table 3**
C, O and O/C of several popular biomass on dry weight (%) basis.

| Biomass type | C (wt%) | O (wt%) | O/C | References |
|---|---|---|---|---|
| Bamboo | 48.39 | 39.21 | 0.81 | [51] |
| Neem | 45.10 | 41.50 | 0.92 | [51] |
| Pine sawdust | 48.62 | 43.20 | 0.88 | [27] |
| Wood (average) | 51.6 | 41.5 | 0.80 | [26,52] |
| | 52.1 | 41.2 | 0.79 | |
| Miscanthus | 48.1 | 42.2 | 0.87 | [1,26] |
| | 49.4 | 43.93 | 0.88 | |
| Switchgrass | 49.6 | 43.4 | 0.87 | [53] |
| Agricultural residues | 49.9 | 42.6 | 0.85 | [52] |
| Soya husk | 45.4 | 46.9 | 1.03 | [52] |
| Rice straw | 41.4 | 39.9 | 0.96 | [26,52] |
| | 48.2 | 45.1 | 0.93 | |
| Sugarcane Bagasse | 44.80 | 39.55 | 0.88 | [54] |
| Microalgae grown in laboratory (*Chlorella* sp.) | 47.54 | 38.63 | 0.81 | [24] |
| Microalgae (*Oscillatoriasp.)* | 37.7 | 38.34 | 1.01 | [19] |
| Microalgae grown in algae farm (*Tetraselmissuecica*) | 48.20 | 21.10 | 0.43 | [46] |
| Microalgae grown in laboratory (*Chlamydomonasreinhardtii*) | 41.23 | 41.3 | 1.00 | [30] |

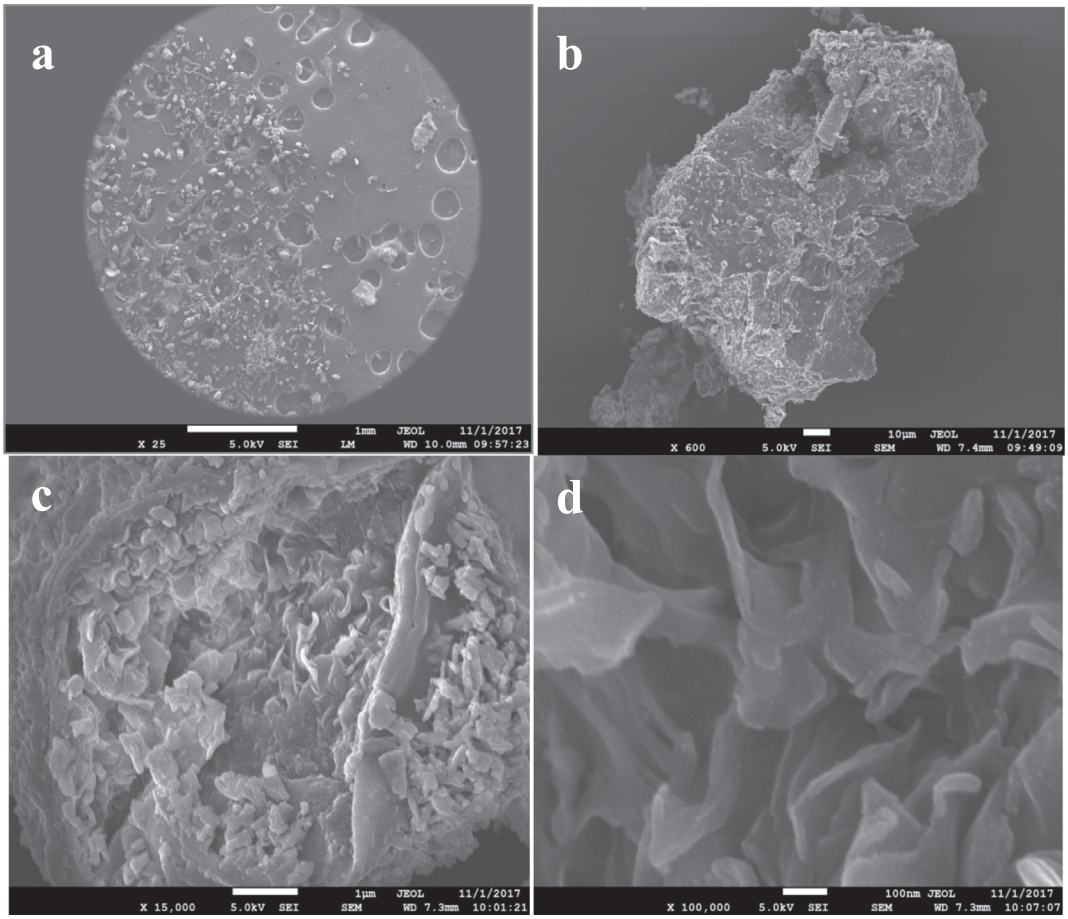


**Fig. 1.** Scanning electron micrographs taken from top view of microalgae pellet with carbon coated specimens at low voltage (5.0 kV) secondary electron image (SEI) detector, (a) view by light microscopy (LM) with working distance (WD) = 10 mm, scale bar = 1 mm, 25x (b) view by scanning electron microscopy (SEM) with WD = 7.4 mm, scale bar = 10 μm, 600x (c)view by SEM with WD = 7.3 mm, scale bar = 1 μm, 15000x (d)view by SEM with WD = 7.3 mm, scale bar = 100 nm, 100000x.

**Table 4**
Elemental Analysis of microalgae and microalgae ash (dry basis) by SEM-EDX.

| Elements | Sample type | Weight (%) | Atomic (%) |
|---|---|---|---|
| Carbon (C) | Microalgae | 30.30 | 41.28 |
| | Ash | 21.54 | 33.11 |
| Oxygen (O) | Microalgae | 40.87 | 41.80 |
| | Ash | 40.15 | 46.34 |
| Nitrogen (N) | Microalgae | 6.36 | 7.43 |
| | Ash | 1.75 | 2.31 |
| Calcium (Ca) | Microalgae | 13.22 | 5.40 |
| | Ash | 19.40 | 8.94 |
| Iron (Fe) | Microalgae | 0.86 | 0.25 |
| | Ash | 1.18 | 0.39 |
| Sulphur (S) | Microalgae | 0.32 | 0.16 |
| | Ash | 0.55 | 0.32 |
| Aluminium (Al) | Microalgae | 1.00 | 0.60 |
| | Ash | 1.53 | 1.05 |
| Silicon (Si) | Microalgae | 3.62 | 2.11 |
| | Ash | 11.03 | 7.25 |
| Tungsten (W) | Microalgae | _ | _ |
| | Ash | 2.87 | 0.29 |
| Nickel (Ni) | Microalgae | 3.46 | 0.96 |
| | Ash | _ | _ |
| O/C ratio | Microalgae | 1.34 | 1.01 |
| | Ash | 1.86 | 1.40 |

C) are directly correlated with energy content of a solid fuel and usually content of oxygen presence causes low energy content. As a result, higher O/C reduces energy content in biomass. In this experiment, the atomic weight of C, O and O/C were 41.28%, 41.80% and 1.01, respectively. The O/C atomic ratio for this sample was slightly higher than other energy crops such as pine sawdust (0.89) as well as other microalgae species grown in fresh water in laboratory such as Chlorella sp. (0.6) [24] albeit nearby ranges with some energy biomass residue like sugarcane bagasse (0.58–0.99), rice straw (0.38–1.07), miscanthus (0.58–0.92) and others [44]. To note, fossil fuel accommodates much higher energy compared to biofuel because of high C, low O and O/C ratio and the elemental analysis of bituminous coal (C: 72.82%, O: 17.24% and O/C: 0.23) manifested this attribute (Table 5). The atomic weight of C and O in ash of biomass were 33.11% and 46.34%, respectively and that was proficient for re-combustion as well as can be the further researched for feasibility of activated carbon [45]. The N weight for *Stigonematales* sp. was 6.36% alike with N component of other microalgae species such as Chlorella sp. (6.73%) [24], *Oscillatoriasp.*(4.7%) [19], *Tetraselmissuecica* (8.7%) [46] and *Chlamydomonas reinhardtii* (8.81%) [30].

**Table 5**
Elemental analysis of experimented coal.

| Elements | C (%) | O (%) | N (%) | Al (%) | Si (%) | Ca (%) | O/C |
|---|---|---|---|---|---|---|---|
| Weight | 67.63 | 21.33 | 10.50 | 0.33 | 0.08 | 0.14 | 0.31 |
| Atomic | 72.82 | 17.24 | 9.70 | 0.16 | 0.04 | 0.04 | 0.23 |

### 3.3.2. Inorganic elements of biomass and ash

Table 4 illustrated the chemical composition of the microalgae

powder pellet and microalgae ash where inorganic constituents were Ca, Fe, S, Al, Si, Ni (only for microalgae) and W (only ash). Microalgae species of this study incorporated quite significant amount of trace elements since they grew drain-water (contained pollutants) habitats and accumulated inorganic elements as rich supplements readily for survival and growth. Previous studies also emphasized on trace metals (e.g. N, P, S, Fe,Ca, Na, Si etc.) utilization by microalgae for its' habitat along with water purification and waste accumulation purposes. Microalgae grown in wastewater typically contain abundant inorganic components than fresh and marine water as well as the species cultured in laboratory and controlled environment [47]. Based on [48], all biomass generally include nutrients such as N, P, Na, K with major components like Ca, Mg, Si and minor components like Mo, Zn, Al, Fe, Cu, Mn, Cl. Na, Ca, K, Mg, P are also notable as alkali metal contents and they play vital role for thermo-chemical conversion of any biomass. Alkali metal contents react with intrinsic Si of biomass and turn the ash into mobile and sticky liquid phase which blocks the airways of the boilers in power plants as well as furnace. As consequences, low alkali metal components are more conductive for the miscellaneous biomass combustion process, though biomass cannot be expected without incorporation of these elements [26]. *Stigonematales* sp. of this study presented a quite large amount of Ca for the case of both samples: raw biomass and ash almost like woody energy crops and higher than agricultural residues, straw, herbaceous crops. For instance, previously EDX of nipa palm resulted that nipa palm frond, shell, husk and leaf ash contained 0.2%-0.6%Ca (dry weight) which was negligible compared to the studied sample ash (19.40%) [48]. The inorganic elements (%) inflated in amount after combustion where organic compounds C, O, N decreased in amount. Apart from this, microalgae presented 3.46% Ni in dry biomass though in ash, Ni was absent and W was present with 2.87% which is a quite rare component in biomass ash. S content in raw biomass was 0.32% which was nearly similar range with other microalgae species such as *Oscillatoria* sp. (0.46%) [19] and *Tetraselmis suecica* (0.51%) [46] albeit the value was higher than the average wood plants (0.1%), miscanthus (<0.1), agricultural residues (0.1%) like wheat, rice and barley straw [26]. Fe, S, Al, Si of this ash sample were 1.18%, 0.55%, 1.53% and 11.03%, respectively which was more than usual energy crops (e.g. nipa palm) ash elements such as Al (0.1%), S (0.3%–0.8%), Si (0.3%–0.8%) [48]. Si is considered the superior component of ash which contributes crucially to slugging, fouling and environmental pollution as well as induces corrosion in furnace during combustion [1]. The total (3.62%) Si of biomass has been elevated after combustion and increased at 11.03% in ash what linearly indicated technical impediments. However, coal studies mentioned that bituminous and lignite coals used for coal industries exhibited 26.98%–36.53% Si of the total ash content after coal combustion [40]. In comparison with this Si content, microalgae ash produced quite low ash, 11.03% which is expected to be tolerated in existing coal-powered operations.

Besides, the towering rate of Si with other alkali metal constituents of this sample also projected slight high amount of sticky ash, fouling and corrosion in the furnace though sometimes chemical leaching enhances combustion intermediaries for biofuels [26,48].

#### 3.3.3. Organic-inorganic elemental analysis of experimented bituminous coal

The bituminous coal of this set of experiments comprised of small O/C, 0.23 alike other bituminous coal O/C ratio (0.2) and this short O/C ratio denoted high heating value of experimented coal [27]. Table 5 represented the result of elemental analysis of bituminous coal. The dry basis weight of C and O were 67.63% and 21.33%, respectively, which was also a nearby range with other bituminous coal (C: 73.1%, O:8.7%) but N (10.50%) was higher compared to other studies (N: 1.4%). The inorganic elements of coal were negligible compared to microalgae biomass since bituminous coal is fossil compound and composed of higher C–C bond than O–C bond [26].

### 3.4. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (Fig. 2) revealed the weight loss stages of *Stigonematales* sp. with temperature in between ambient temperature, 24 °C–850 °C. Derivative thermogravimetric (DTG) curve (Fig. 2) has differentiated thermogravimetric values measuring weight loss of the sample during heating process from 24 °C to 850 °C. DTG of this study has diagrammed the maximum peaks of degradation at various temperatures for clear visualization of different combustion stages. Simultaneously differential scanning calorimetry (DSC) curve in Fig. 3 presented the sample mass loss versus heat flow of this TG analysis. First stage was under 150 °C where moisture content and gas desorption took place and portrayed the hygroscopic characteristics of microalgae biomass. Stage 1 in TG curve illustrated the moisture content approximately 4.5% and later, H content (3.15%) was simulated by Eq. (3) where theoretically moisture and H content were simulated as 3.4% and 1.22%, respectively at 105 °C. TG analysis manifested the precise content of moisture and H as well as contrasted the actual result with the theoretical approach [24]. At stage 2 ($150\,^{\circ}C < T < 350\,^{\circ}C$), the decomposition of low molecular solvent and products were observed and consistently 9.5% weight loss was prevailed. TG study of *C. reinhardtii* [30] claimed that portion of cellular lipid and photosynthetic pigments like chlorophyll A and B were degraded at 190 °C under stage 2. Since the sample species was blue-green in colour, it was assumed that the pigmentation would be degraded in this stage. Thermal decomposition arose roughly at 7% within 350 °C–500 °C (stage 3) where usually the thermo oxidative ($O_2$ content) decomposition starts to initiate. At $500\,^{\circ}C < T \leq 800\,^{\circ}C$, the weight loss of biomass turned very slow with 7.5% and carbonaceous matters de-volatiled. Usually at higher temperature like 500 °C or above, carbohydrates (cellulose, hemicelluloses, lignin) and fatty acid chains are deteriorated as well as de-volatilization is obtained [24,27,30,49]. From 800 °C to 850 °C (stage 5), final weight loss and complete volatilization took place and residue/ash was left. The TG curve dropped from 71.5% to 60.5% within 800°C–850 °C and combustion has been stopped with ash content (AC%), 39.5%. The highest temperature for combustion was set till 950 °C but the mass loss of biomass stopped at 850 °C what elucidated the highest temperature to combust biomass entirely. This weight loss (%) versus temperature curve revealed the total volatile content and ash content of *Stigonematales* sp. sample. De-volatilization has been initiated after the moisture removal till the final weight loss what drove the volatile matter (95.5%–60.5% weight loss). The result by TGA was presented at Table 6.

The combustion process was performed initially under an inert condition with the presence of Ar gas for degradation of the experimented microalgae. The low heating rate 10 °C/min was implemented since previous research on different species of microalgae demonstrated that the differences of mass loss of microalgae species was consistently slow throughout the burning process and low heating rate distinguished the peaks in DTA curve properly where high heating rates manipulated peaks to overlap [24,30]. After combustion, the green microalgae powder was transformed into the soft grey (sand colour) ash. Fig. 4 illustrated the samples before and after combustion of microalgae by the TGA.

At the 10 °C/min heating rate, other microalgae such as *Chlorella* sp. was combusted steadily and the final weight loss was lower compared to 20 °C [24] where *Chlamydomonas reinhardtii* presented no distinction for combustion and weight loss difference

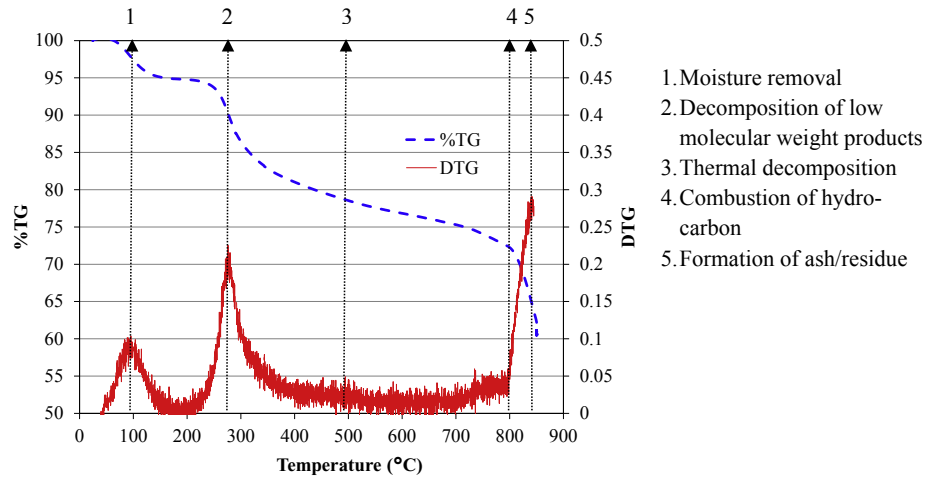


**Fig. 2.** Thermogravimetric curve (TG-DTG) for dry microalgae biomass at 10 °C/min.

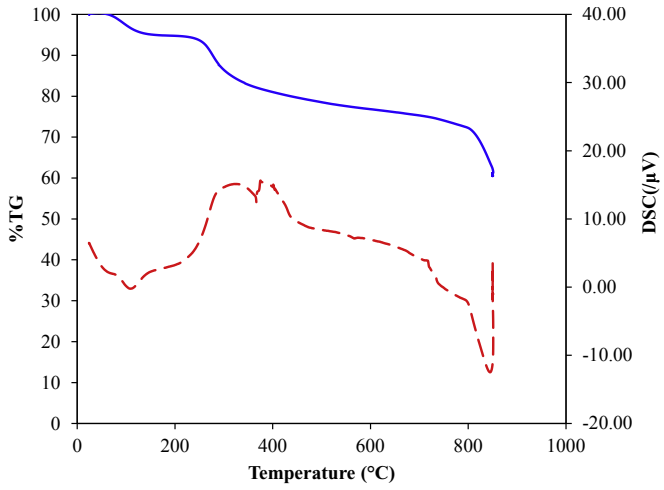


**Fig. 3.** Differential scanning calorimetry (TG-DSC) for dry microalgae biomass at 10 °C/min.

**Table 6**
Thermal decomposition analysis by TGA.

| Sample | MC% | H% | VM% | AC% | FC% |
|---|---|---|---|---|---|
| *Stigonematales* sp. | 4.5 | 3.15 | 35 | 39.5 | 21 |

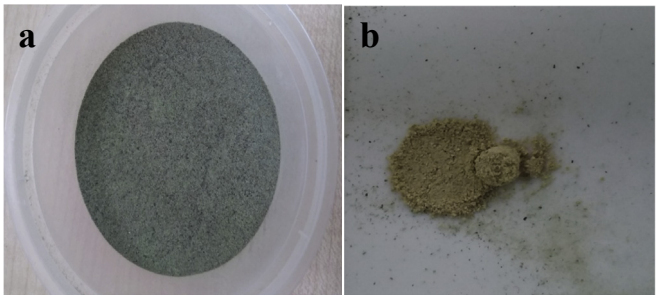


**Fig. 4.** *Stigonematales* sp. powder before (a) and after (b) combustion.

with several heating rate like 5 °C, 10 °C, 20 °C and 30 °C [30]. Thus 10 °C/min can be projected as the most favourable heating rate for consistent combustion and economical aspect. Several freshwater grown microalgae species fabricated lower ash and higher volatile matter than *Stigonematales* sp. since the current sample was collected from drain water and accumulated high organic compounds unlike species in a controlled environment [24,30]. Table 6 demonstrated the sample powder impregnated with insignificant moisture, which was great factor for biomass to fuel conversion and moisture content also revealed moderate hydrogen content as well. 39.5% ash can be counted quite a large portion of AC content but for naturally grown microalgae, especially in wastewater, ≥30% ash content is usual due to the abundant inorganic elements and impurities (sand, clay and others) mixed with microalgae [1]. 35% volatile matter of this species devalued the amount of hydrocarbon, methane, hydrogen and combustible gas presence unlike woody biomass and fossil fuel. However, fixed carbon, 21% can be counted for adequate and continuous heat generation during the combustion process [26,37,50].

## 4. Conclusions

*Stigonematales* sp. exhibited several significant traits to generate bioenergy as a renewable source. The characterizations of *Stigonematales* sp. demonstrated the basic data for energy production, biomass handling and storage. The experimental results were also ensuring that the microalgae from waste biomass can be used as bioenergy feedstock coupled with wastewater treatment and the greenhouse effect minimization by $CO_2$ mitigation. The pure biomass characterization determined the thermo-physical conversions at several stages of burning session. Microalgae-bituminous coal blend experimental results manifested a great impact on heat elevation as a supplement in heat and electricity generation industries by coal. The microalgae, *Stigonematales* sp. from drain-water grows naturally without any cost, only labour cost will be required for collection and pre-treatment to blend with coal for generating heat and electricity in large-scale application and for that purpose, a comprehensive techno-economic analysis and life-cycle assessment will be conducted in further research.

## Acknowledgement

The award of Brunei Darussalam Govt. Scholarship to Nazia Hossain and the Faculty of Integrated Technologies, Universiti

Brunei Darussalam are gratefully acknowledged. The SEM laboratory of Geology Department and Research Lab mg-16 of Physics Department are acknowledged for their support to run SEM-EDX and TG-DTA analyses. The authors would also like to acknowledge Universiti Tenaga Nasional Internal Grant (UNIIG 2017) (J510050691) for supporting this research. Authors like to thank Ashfaq Ahmed, Nikdalila Radenahmed, Shammya Afroze, Syarif Hidayat, Mohd Yameany Hj. Rosli and Muhd Nur'naqiuddin Bin Haji Osman for their cooperation and assistance during the experiments.

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