Research Article

Thermogravimetric Analysis of Marine Macroalgae Waste Biomass as Bio-Renewable Fuel

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Received 15 July 2022; Accepted 24 August 2022; Published 29 September 2022

Academic Editor: Ajaya Kumar Singh

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Macroalgae are considered as the 3rd generation of biofuels and a future feedstock for biorefinery. This research aims to provide simple and dependable analytical techniques for measuring the thermal characteristics of dried seaweed. The main objective was to investigate the thermal characteristics of four seaweed species utilizing a thermogravimetric analyzer. The seaweeds Gracilaria fisheri, Caulerpa lentillifera, Ceramium rubrum, and Eucheuma cottonii were collected from the Pahang state of Peninsular Malaysia. The calorific value of the samples was revealed by using a calorimeter. Ceramium rubrum showed the highest calorific value, while Gracilaria fisheri had the most negligible calorific value among the selected samples. The thermogravimetric analysis (TGA) data revealed that the most significant weight loss for this biomass occurred between 160 and 300 °C for the selected species. Gracilaria fisheri has shown the highest decomposition with the minor residue at 30.26%, whereas Caulerpa lentillifera has a slow weight loss rate in the mentioned range. SEM analysis has been used to perform the morphology of samples, which shows differences in the concentration of epiphytic diatoms with different structural shapes. Based on the results, macroalgae is a promising sustainable biomass feedstock for biofuel application.

1. Introduction

Seaweed is a multicellular, macroscopic, eukaryotic, and autotrophic creature known as marine macroalgae or seaweeds. Based on the color of the thallus, they are classified into three big and separate groups: Chlorophyta (green algae), Rhodophyta (red algae), and Ochrophyta-Phaeophyceae (brown algae). Even though macroalgae rather than microalgae have been the subject of many recent studies, the global market for macroalgal nonfuel products is currently 100 times greater than microalgae in terms of wet tonnage [1–3]. Macroalgae have a high water content, a high carbohydrate content (25 to 50%), a high protein content (7 to 15%), and a high lipid content. They are considered as suitable sources (1 percent to 5 percent) for the generation of biodiesel, bioethanol, and biohydrogen [4–6]. There is potential to consider carbon sequestration related to seaweed growth in calculating the carbon balance of macroalgae biofuel from aquaculture [7]. Their cultivation along the coasts (China and the United States) is projected to sequester around 1 billion tonnes of carbon/year [8].

With a rapid proliferation and strong CO₂ fixation, algal biomass is one of the most sustainable biomass feedstocks for renewable resources. Algal biomass is the ideal feedstock for next-generation biofuels and chemical synthesis. It is
anticipated to offer a better potential for the production of biofuels than terrestrial lignocellulosic biomass [9, 10].

Microalgae and macroalgae are different types of algae. Because of their high lipid content, microalgae are widely employed in the generation of biofuels. Microalgae thermochemical conversion has also been widely researched, including direct combustion, pyrolysis, direct liquefaction, hydrothermal liquefaction, and gasification [11]. Microalgae have received a lot of interest in the scientific community.

Macroalgae, on the other hand, have clear potential for the development of biofuels, as reported in previous reports [12, 13]. Previous studies have shown seaweed (macroalgae) potentiality as a source of proteins, carbohydrates, minerals, dietary fiber, vitamins, and saturated and unsaturated fatty acids. It can be hydrolyzed to fermentable sugars like glucose and galactose and fermented to ethanol.

Malaysia has a lot of potential to be the global leader in seaweed production because it has many prospective seaweed farming sites. Over time, seaweed production has increased more quickly, and it is now a crucial natural resource for Malaysia’s economic growth. Different methods for biomass conversion into energy products, i.e., biofuels, and bioproducts, are constantly being researched.

Algae thermochemical processing includes complex physicochemical processes. Studying the solid-state degradation kinetics of the feedstock is essential to provide insights into the heterogeneous processes, which are often addressed via thermogravimetric analysis (TGA) [14]. For assessing the pyrolysis behavior of biomass, which is complex chemically due to the existence of several chemical reaction pathways, TGA is one of the most used techniques [15].

Nevertheless, there is currently a limited study on converting these macroalgae (also known as seaweed) into biofuel. Data on the viability of macroalgal biomass for biofuel production is particularly scarce. As previously stated, Malaysia’s tropical weather has provided a perfect environment for a diverse spectrum of algae species. As a result, Malaysia has many algal resources that should be studied further [9]. This study focuses on the viability of macroalgae Gracilaria fisheri, Caulerpa lentillifera, Ceramium rubrum, and Eucheuma cottonii as renewable biomass.

The study’s objective is to characterize the macroalgae waste biomass using various techniques.

(i) Scanning electron microscopy
(ii) Thermogravimetric analysis
(iii) Calorimetry

2. Materials and Methods

2.1. Sample Collection. Macroalgae samples were collected from the Pahang state, east coast of Peninsular Malaysia. The samples of fresh macroalgae were cleaned with deionized water several times to get rid of any sand or debris sticking to them. Later, they were dried for 24 hours at 80°C in a drying oven. In preparation for further examination, the dried samples were crushed and sieved before being placed in zip-lock bags.

Sample A is Gracilaria fisheri, the third largest genus of class Rhodophyta.
Sample B is Caulerpa lentillifera, a type of seaweed from the Chlorophyta group known as sea grapes.
Sample C is Ceramium rubrum (Rhodophyta: Florideophyceae) is a marine alga.
Sample D is Eucheuma cottonii, a red macroalgae, one of the most numerous species on Sabah’s east coast (Malaysia).

2.2. Thermo-Physical and Chemical Analysis

2.2.1. Scanning Electron Microscopy (SEM). SEM technique was used to analyze the surface morphology, and the structural rectangle, triangle, radial hexagonal, rod, and spherical shapes were estimated. A scanning electron microscope (SEM), model Hitachi S-3400N, with an acceleration voltage of 10 kV, was used to examine the algal samples’ morphology.

2.2.2. Thermogravimetric Analysis (TGA). TGA has been used to describe the biomass pyrolysis characteristics in terms of weight loss caused by a rise in temperature. When a sample is heated at a constant temperature (or rate) in either an oxidative (air) or an inert nitrogen atmosphere, TGA may measure weight increase or loss. A Hitachi high-tech scientific corporation STA series thermal analyzer was used to perform TGA on the sample. Using a thermogravimetric analyzer, the analysis was carried out in aluminum pans with a dynamic nitrogen atmosphere at a heating rate of 5°C/min in the temperature range of 25°C–800°C. TGA and DTG were used to examine the thermochemical behavior of biomass during pyrolysis. A continuous supply of pure nitrogen (N2) gas was maintained at a flow rate of 80 mL/ min to provide a suitable environment in the heating chamber. This procedure frequently entails several intricate chemical reactions that happen instantly, which prevents the comprehension of the reaction’s mechanism.

Consequently, thermogravimetric analysis, or TGA, is frequently employed to understand the solid-state breakdown kinetics that occurs during thermal decomposition [16]. The equivalent DTG (derivative thermal analysis) 1st derivative of the TGA curve gives the degradation rate. The right step is often determined using the DTG peak as a characteristic value. DTG is a type of thermal analysis that makes it easier to analyze the weight versus temperature thermogram peaks that occur close together by plotting the rate of material weight change as a function of temperature against temperature.

Each heating test was followed by a separate blank run using an empty pan to establish a baseline. Finally, the weight loss was recorded with the temperature increase, and the TGA and DTG curves were shown.

2.2.3. Calorimetry. The quantity of heat emitted by a substance during combustion is known as the calorific value of that substance. It is impacted by the biomass’s ash and
moisture levels. Ash content reduces a fuel’s calorific value and could be problematic during high-temperature combustion. Moisture in fuel reduces its overall thermal efficiency because a portion of the heat of combustion is used to evaporate the container moisture, lowering the calorific value. Samples of dried seaweed are tested for their calorific values using an IKA C 3000 isoperibol calorimeter.

3. Results

The following sections have discussed the SEM, thermogravimetric, calorific value, and analysis of the macroalgal biomass samples.

3.1. SEM Analysis. Figures 1–5 show SEM micrographs of four different seaweed species samples. The sample had a distinct form and poorly defined pores. This picture depicts several fibrous structures and a modest proportion of irregular-shaped microscopic particles. All morphological analyses were performed at 10 μm and 1 μm. Furthermore, the surface morphology seemed rough, most likely due to the variation in chemical contents.

*Gracilaria fisheri* surface was primarily devoid of epiphytic diatoms, evident throughout the structure. The structures are visibly agglomerated with a rough texture and heterogeneous system, with no flaws such as fractures inside the formations.

*Caulerpa lentillifera* analysis shows rich colonization of elliptically shaped diatoms.

Sample C analysis shows that algae are densely populated with epiphytic colonizers.

Sample D analysis showed a stem-like structure. It offers a branch section with a low amount of epiphytic diatoms.

3.2. Thermogravimetric Analysis. Figures 6–9 show the TGA and DTG curves for seaweeds *Gracilaria fisheri*, *Caulerpa*
lentillifera, Ceramium rubrum, and Eucheuma cottonii under pyrolysis conditions. Like Zhihua Chen et al., three primary phases of biomass degradation are discovered [17]. Thermal degradation stages in TGA for samples A, B, C, and D and their temperature region were observed for weight loss, as shown in (Tables 1–4). Heating rates of 5°C/min were maintained during the analysis. The thermal degradation of four samples of macroalgae occurred in a two-step process, according to the findings. The loss of weight at the beginning of the process can be attributed to the sample's water content evaporating [18] or some light volatile matters [17, 19]. The second stage revealed a significant weight loss due to the primary decay process. This loss is attributable to the disintegration and/or depolymerization of organic algal
components such as lipids, proteins, and carbohydrates. The weight loss of algae between 160 and 300°C is related to carbohydrate breakdown, whereas protein degradation occurs between 320 and 450°C [20]. At stage three, when the temperature reached 800°C, the residue was found above 800°C.

For sample A, the derivative thermogravimetric analysis (DTG) showed a sudden peak in weight loss of 33% which was recorded in a temperature range of 165°C–200°C where the mass loss rate reached a peak value of 131%/°C. The 2nd DTG peak was observed between 702°C and 782°C at a peak mass loss rate of 24.46%/°C. After heating up to 799.5°C, 30.26% of the sample residue was left.

For sample B, two peaks were observed with a mass loss rate of 42%/°C at 51°C and dropped gradually to 5%/°C at 155°C before reaching the 2nd peak to 37%/°C at 185°C and suddenly dropping to 9%/°C at 220°C. At the first peak, a mass loss of 10% was observed and reached a mass loss of
28.54% at the 2nd peak. After heating up to 798.5°C, 37% of the sample residue remained.

For sample C, DTG sharply dropped from 69.96%/°C at 26.81°C to 20.82%/°C at 35.37°C and gradually reached the lowest rate of 4.2%/°C at 187.29°C. Two humps are observed between 181°C and 346 °C with peak mass loss rates of 20.5%/°C and 17.26%/°C. Mass loss of 37% was observed at the 2nd hump peak. After heating up to 798.2°C, 43.64% of the sample residue remained.

For sample D, DTG sharply dropped from 31.22%/°C at 28.97°C to 10.48%/°C at 35.37°C and gradually reached the lowest rate of 3.75%/°C at 181.83°C and sharply increased to 30.16%/°C at 221.96°C and progressively reached to a lowest mass loss rate of 2.05%/°C at 562°. Mass loss of 21.61% was observed at peak DTG. A slight increase in DTG was observed between 664 °C and 799 °C. After heating up to 799°C, 36.77% of the residue remained.

3.3. Calorific Value Analysis of Macroalgae Biomass. When assessing a biomass sample's potential for use as fuel, its calorific value is frequently a crucial consideration. Table 5 shows the elemental analysis results of the algal biomass samples. Compared to other renewable biomass feedstocks and traditional fossil fuels, seaweed (in this study) has one of the lowest calorific values. Overall, biomass has a lower calorific value than fossil fuels. In other words, sustainable biomass feedstock produces significantly less energy (per same mass) than fossil fuel. However, utilizing macroalgae biomass has several benefits over fossil fuels, such as sustainabilty and reduction in CO₂ emissions. According to prior research, macroalgae have the lowest calorific value among several other biomass feedstock, including soybean (38.3 MJ/kg),

Table 1: Different stages of the TGA for Gracilaria fisheri in N₂ environment.

<table>
<thead>
<tr>
<th>Phases</th>
<th>Phase 1</th>
<th>Phase 2</th>
<th>Phase 3</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>30 to 168.7</td>
<td>168.7 to 222.3</td>
<td>222.3 to 800</td>
<td>171 (peak)</td>
</tr>
<tr>
<td>Weight loss (%)</td>
<td>16</td>
<td>39.59</td>
<td>14.15</td>
<td>30.26 (residue)</td>
</tr>
</tbody>
</table>

Sample A: Gracilaria fisheri.

Table 2: Different stages of the TGA for Caulerpa lentillifera.

<table>
<thead>
<tr>
<th>Phases</th>
<th>Phase 1</th>
<th>Phase 2</th>
<th>Phase 3</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>30 to 173.1</td>
<td>173.1 to 287.2</td>
<td>287.2 to 800</td>
<td>185 (peak)</td>
</tr>
<tr>
<td>Weight loss (%)</td>
<td>24.85</td>
<td>13.26</td>
<td>24.89</td>
<td>37 (residue)</td>
</tr>
</tbody>
</table>

Sample B: Caulerpa lentillifera.

Table 3: Different stages of the TGA for Ceramium rubrum.

<table>
<thead>
<tr>
<th>Phases</th>
<th>Phase 1</th>
<th>Phase 2</th>
<th>Phase 3</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>30 to 186.5</td>
<td>186.5 to 307.2</td>
<td>300 to 800</td>
<td>221.96 (peak)</td>
</tr>
<tr>
<td>Weight loss (%)</td>
<td>16.14</td>
<td>18.18</td>
<td>22.04</td>
<td>43.64 (residue)</td>
</tr>
</tbody>
</table>

Sample C: Ceramium rubrum.

Table 4: Different stages of the TGA for Eucheuma cottoni.

<table>
<thead>
<tr>
<th>Phases</th>
<th>Phase 1</th>
<th>Phase 2</th>
<th>Phase 3</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>30 to 192.8</td>
<td>192.8 to 300</td>
<td>300 to 800</td>
<td>221.96 (peak)</td>
</tr>
<tr>
<td>Weight loss (%)</td>
<td>13.86</td>
<td>21.51</td>
<td>27.86</td>
<td>36.77 (residue)</td>
</tr>
</tbody>
</table>

Sample D: Eucheuma cottoni.

![Figure 9: TGA curve and DTG curve for Eucheuma cottoni.](image)
Analysis and characterization lead to the following conclusions: physical and chemical characteristics. Subsequently, the sample analyze the four macroalgae waste samples for their thermo-tainable biomass resource. Hence, this study attempted to biofuel sources, macroalgae are gaining attention as a sus-

Among recent developments in cellulosic and noncellulosic 

4. Discussion

Four different samples of macroalgae waste biomass have been investigated in this paper for morphology, thermal characteristics, and calorific value using SEM, TGA, and calorimeter toward the potentiality of biofuels or bio-products. Results revealed a difference in the morphology of the seaweeds, which may be due to the chemical composition. This study’s most significant number of epiphytic diatoms is comparable to those discovered on macrophytes from different depths and areas [23–26]. Further, each sample was analyzed under thermogravimetric analysis for thermal characterization. The study revealed a difference in residual percentage for each material after reaching 800°C, which is affected by the following factors: chemical composition, density, crystallinity, and porosity. Macroalgae, like microalgae, have a water content between 74 and 89 percent [27–29]. Drying a high amount of water needs higher energy requirements. Drying is an expensive, time-consuming, and energy-intensive process. Heat is used in thermochemical processing procedures to transform biomass. These include techniques like rapid pyrolysis and carbonization for creating solid fuels, gasification for producing gaseous products, and pyrolysis and hydrothermal liquefaction for producing liquid fuels. Although pyrolysis has been proved for a wide range of biomass, it is less appropriate for processing high-moisture feedstocks because of the significant energy loss associated with evaporating water at atmospheric pressure [30]. Drying can be prohibitively costly for biomasses with high water content, such as microalgae and macroalgae, as well as some tropical grasses [31]. When it comes to high-moisture biomass, HTL has several significant benefits. Wet feedstocks like micro- and macroalgae are ideally suited for hydrothermal liquefaction, which significantly reduces the energy needs associated with feedstock drying [32, 33], lowering the oxygen level and increasing the energy content of the liquid products that are produced [34] concerning the oils produced by pyrolysis.

5. Conclusions

Among recent developments in cellulosic and noncellulosic biofuel sources, macroalgae are gaining attention as a sustainable biomass resource. Hence, this study attempted to analyze the four macroalgae waste samples for their thermophysical and chemical characteristics. The subsequent sample analysis and characterization lead to the following conclusions:

(i) SEM analysis revealed that the morphological structure and number of epiphytic diatoms varied considerably among the four seaweed samples. The variation is primarily due to the specific biochemical composition of seaweed. However, the cell structures remained intact with increased pores and residual materials.

(ii) The calorific value of the four samples has been analyzed using a calorimeter. Sample C: Ceramium rubrum has shown a higher heating or calorific value of 10.45 MJ/kg compared to the lowest Sample A: Gracilaria fisheri with the calorific value of 7.26 MJ/kg. High ash and moisture contents resulted in lowering the practical calorific value. A higher amount of drying may be needed to achieve a comparable heating value.

(iii) Macroalgae decomposition takes place in three significant steps of degradation that can be observed in TGA. All the samples exhibited a similar stage of decomposition, despite having varied compositions. Results showed that the thermal degradation rate of the Gracilaria fisheri tends to be higher than the other species, with 39.59% mass loss during phase 2. In contrast, Caulerpa lentillifera has the lowest weight loss of 13.26% during phase 2. The highest volatile matter and fixed carbon are desirable for biofuel production.

(iv) However, further study is required to assess the selected macroalgae’s potential as a renewable fuel. This research can provide preliminary research data for further investigation.

(v) The inclusion of macroalgae species as a bioenergy source will assist in diversifying the countries’ energy dependency and reduce the negative environmental issues associated with conventional energy crop production like oil palm.

Data Availability

The data used to support the findings of this study are included within the article.

Disclosure

This manuscript’s opinions, facts, insights, and discussions solely involve the authors. It does not necessarily reflect the policy and standpoint of any organization directly or indirectly.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

The authors are grateful for the PGRS 210349 grant by Universiti Malaysia Pahang. This manuscript’s opinions, facts, insights, and discussions solely involve the authors. It does not necessarily reflect the policy and standpoint of any
organization directly or indirectly. The authors are not responsible for any consequences of the information presented in this work.

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