Utilization of Macroalgae via Thermochemical Process for Biochar Production

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Abstract

Nowadays, environmental pollutions are increasing due to high amount of consumption of fossil based fuels and growing industry. Because of this pollution, utilizing renewable energy sources draws attention and the researches which made for elimination of this pollution has gained great importance. In this context, utilizing macroalgae is one of the solutions for both alternative fuel production and usage in various industry fields as chemistry, agriculture and environment. Macroalgae or seaweeds are plants which are adapted to the marine life, often located in coastal areas. They are classified as brown seaweeds, red seaweeds and green seaweeds according to their pigments. They are abundant resources due to their easily proliferation and accumulated greatly as waste in coastal areas, so they are collected regularly by coastal municipalities and sent to waste disposal. Macroalgae can be converted to algal biochar via thermochemical processes and can be used as energy source, activated carbon and soil improver. In this study, macroalgae in coastal regions of Marmara Sea were collected and carbonization process was performed to investigate temperature effect on product yield in temperatures of 200, 300, 400, 500 and 600°C, nitrogen flow rate of 600 ml/min and at a heating rate of 20°C/min and the highest biochar yield was obtained at the carbonization temperature of 200°C. It can be said that algae shouldn't be disregarded for biochar production and should be considered for utilization in the present and future.

Key words: Algae, Macroalgae, Biochar, Biomass, Carbonization

1. Introduction

In recent years, due to increase in population, developing industrialization and consumption patterns are accelerating environmental pollution. In order to prevent this, many studies are conducted and solution offers are proposed. One of these solutions is using algae with different utilization methods to obtain valuable products and use in various usage areas such as treatment of wastewaters, agriculture and chemistry. Algae can be defined as prokaryotic or eukaryotic primitive organisms that have simple reproductive system and photosynthetic pigments to carry out photosynthesis [1]. They comprise a wide range of organisms such as single cell microalgae and seaweeds which can be complex multicellular organism that can be reached to meters in length [2]. Algae can be divided in two main groups as microalgae and macroalgae according to their morphology. Macroalgae are also classified as green, red and brown algae according to their pigments [3]. While microalgae contain more lipid and cultivated in artificial pools and bioreactors, macroalgae mostly grow in seas, lakes and wastewater basins spontaneously [2]. Macroalgae are ecologically and economically significant livings due to contribution to environment by producing O_2 with utilizing CO_2 and have nutritional substance for usage as food [4]. In addition to that, they can be used for wastewater treatment with their heavy metal, phosphorous and nitrogen absorption capability. However nowadays, lots of macroalgae species

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are cultivated for food and cosmetic industry. Algae can grow under optimum temperature, space and illumination and while they grow, turbidity of water increase because of the activity of algae, penetration of light is prevented and some organism live in deep parts of the water may die [5]. Today, pollutants like nitrogen which resulting from consumption habits, domestic and industrial wastes forms nutrition group for algae and this causes cultivation of algae rapidly [6]. Turkey is surrounded by seas on three sides and intensive cultivation of algae in these seas makes them an important source of biomass. *Ulva* kind macroalgae which is the biomass used in this study, especially are found in Marmara, Black and Aegean Sea [7]. These macroalgae need light for their growth and because of this, they spread out the upper surface of the water. They perform better structural development in the nitrogen rich polluted areas.

In this project study, *Ulva lactuca* species which were collected from coastal areas of Marmara Sea were utilized to evaluate their potential for biochar production via thermochemical process. Although algae are mostly used for biodiesel and bioethanol production, macroalgae, which are found in coastal areas and are considered as wastes, can be utilized in biochar production. Production of algal biochar is based on the carbonization process which is one of the conversion methods degrading dry biomass to biochar thermochemically in oxygen-free environment [8]. Obtained product, biochar is a solid material which has high carbon content and acquired by thermal decomposition of organic material subjected to low temperature (<700 °C), in the inert gas atmosphere. Biochar can be used in various areas such as energy, metallurgical and chemical areas. It can be an alternative against conventional fuels depending on their great fixed carbon content and high calorific value [9]. Besides, it can amend the physical, chemical and biological properties of soil and can improve nutrient and water holding capacity and plant growth [10]. Gaskin et al., have studied the cation exchange capacity of different biochar samples produced from peanut shell pellets, pine shavings, pine sawdust pellets, pine bark and oak shavings on soil [11]. It was found that, biochars from peanut shell pellets had the highest cation exchange capacity and increased water holding capacity of soil. Rondon et al., investigated the effects of different amounts of biochar application (0, 30, 60 and 90 g kg^{-1}) on biological nitrogen fixation of beans. It was resulted with an increase on nitrogen amount from 50% to 72% by adding 90 g kg^{-1} biochar [12]. As an adsorbent, it can be used for purification process by applying chemical activation. During chemical activation, the source material is impregnated with certain chemicals, typically an acid, a strong base or a salt such as phosphoric acid, potassium hydroxide, calcium chloride and zinc chloride. Activated carbon which is obtained from this process can be utilized in different usage areas such as water treatment, food and medical industries.

In the literature there are studies about factors that affect biochar production from algae. These analysis are carried out under two titles as characteristics of algae and carbonization parameters. These researches on biochar production from algae are performed under different conditions and characterization of algal biochar. Temperature, heating rate, properties of gas atmosphere, particle size and properties of algal biomass are the main important parameters investigated in the researches. Temperature, one of the most effective factor affects the yield of algal biochar significantly, causes differences in chemical structures of algal biochar. Recent studies show that increases in temperature affects biochar yields, the reactivity of biochar and the ratio of H/C and O/C in algal biochar, negatively [13]. Generally, the maximum yields of algal biochar were obtained at the temperatures of 350-550°C, in these studies [14, 4, 15, 16]. The heating rate is another important parameter affects yield and chemical structure of biochar. Nevertheless, this parameter is not investigated alone to observe its effect on biochar properties so it should be considered as a function of retention time and temperature during experiments [13, 17]. The properties of gas atmosphere such as inert and reactive gas, is an expression of presence or absence of the substances that affect the process. Different gas atmosphere can cause differences in the amount and quality of biochar obtained via carbonization process. The catalyst can be defined as substances that increase the reaction rate of the process by lowering the activation energy. These materials can be removed from the reaction after the process. Besides, they can alter the mechanism of reaction [13]. Particle size of the algal biomass is another parameter affecting the yield of biochar. When particle size of biomass samples increases in carbonization process, yield of solid material increases; yet, yields of liquid and gaseous products decrease. The reason is that the increase of partical size causes the temperature variation in particles [18-20]. Because of this, in order to increase the yield of the solid product in carbonization process, macroalgae biomass samples are preferred instead of microalgae [21]. Characteristics of algal biomass also affect both the conversion process and the product yield. The mineral content of algae is higher than many terrestrial plants and nutrients from animals [22]. Thermochemical conversion processes have not considered for utilization of algae owing to high moisture and alkali metal content. Since the amount of these minerals can cause some problems like slagging, fouling and other ash related problems, this restricts its usage as fuel in combustion and gasification. On the other hand, availability of alkali metals in algal biomass improves the biochar yield [23].

In this article, an experimental study of biochar production from *Ulva lactuca* macroalgae is presented. TG analysis was also performed to observe the thermal decomposition of macroalgae.

2. Materials and Method

Ulva lactuca, one of the green macroalgae species, was selected for the production of algal biochar and evaluation of the conversion potential. This species of macroalgae that were collected from coastal areas of the Marmara Sea were washed, dried at the temperature of 70°C for 18 hours and then separated into small pieces. The carbonization experiments were performed in "Protherm" model split type reactor which is a horizontal flow pipe type reactor with an inner diameter of 10 cm (Figure 1). Experiments were carried out by using approximately 3.2 gram sample of macroalgae. Before the experiments, inside of the reactor were swept with nitrogen gas in 15 minutes to provide an inert atmosphere. Carbonization process was conducted at temperatures of 200, 300, 400, 500 and 600°C, nitrogen flow rate of 600 mL/min and with heating rate of 20°C/min. When the desired final temperature was reached, samples were hold in 15 minutes at the final temperature. After the reactor was cooled, samples were removed and weighted and the biochar yields were calculated.

Figure 1. Split pipe typed reactor

3. Results

In our experiments maximum biochar yield of macroalgae was found 62% at the temperature of 200°C. As can be seen in Table 1 and Fig 2, after the temperature of 200°C, biochar product yield decreased with increasing temperature in carbonization process. Biochar yield of *Ulva lactuca* was obtained at the lowest value as 36% at the temperature of 600°C. It can be suggested that algal biomass can be utilized effectively via carbonization process and high algal biochar yields can be obtained with less energy input by conducting the process at the low process temperatures. In the literature studies, it can be seen that increase of process temperature affects biochar yields and reactivity of biochar negatively. Choi et al. produced biochar at the temperature of 450°C from *Saccharina japonica* brown alga in a fixed bed reactor. Biochar yield was calculated as 33% [24]. Yanik et al. obtained the yields of algal biochar as 29-36% in carbonization process which conducted at the temperature of 500°C in a fluidized bed reactor [25]. Kebelmann et al. reported that the maximum degradation of macroalgae occurs at the temperatures of 220-320°C [26]. The results obtained from our study are in agreement with these studies for biochar production.

Table 1. Biochar amounts and yields obtained in different carbonization temperatures (Heating rate: 20 °C/min, nitrogen flow rate: 600 ml/min)

Temperature (°C)	***Sample Weight (gr)***	***Biochar Weight (gr)***	***Yield (%)***
200	3,2	2,00	62
300	3,2	1,60	50
400	3,2	1,35	42
500	3,2	1,25	39
600	3,2	1,15	36

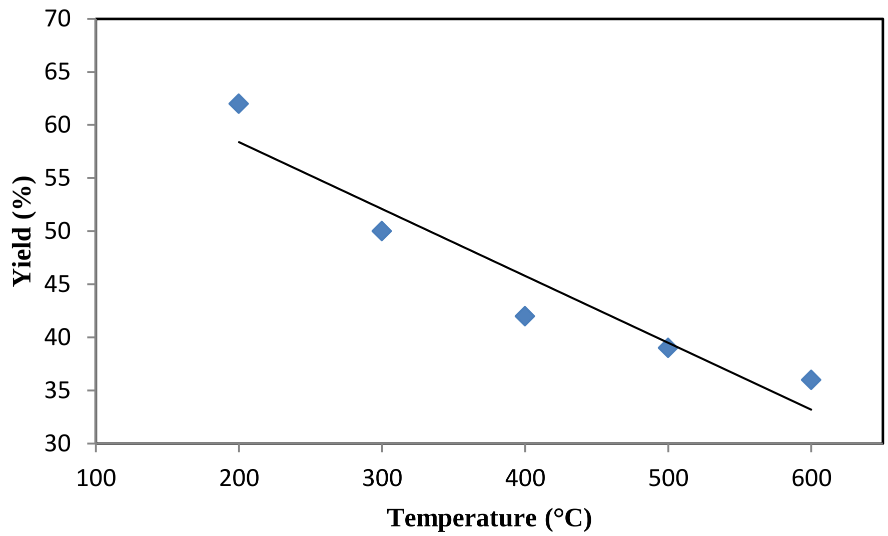

Fig 2.Carbonization temperature effect on biochar yield values

3.1. Characterization of *Ulva lactuca* via thermogravimetric analysis (TGA)

Thermogravimetric analysis results of biomass samples were obtained with thermogravimetric analyzer (TA Instrument) and results were given in Fig 3 and 4. Analysis were performed under the conditions of nitrogen atmosphere using approximately 5-10 mg sample, which was heated up to 1300°C with a heating rate of 10, 25 and 50°C/min and carrier gas flow of 100 mL/min. Table 2 shows conditions and results of thermogravmetric analysis for *Ulva lactuca.* As Fig. 3 shows TG and DTG curves of thermogravimetric analysis of *Ulva lactuca* in nitrogen atmosphere at the heating rate of 10 C/min, Fig.4 shows that the composition of TG curves of *Ulva lactuca* at the different heating rates such as 10, 25 and 50 °C/min. When the thermogravimetric analysis was carried out to 1300°C, the final weight was found as 7,63% (0,4898 mg).

Table 2. TGA conditions and results for *Ulva lactuca* (Temperature: 1300 °C, Purge gas flow rate: 100 ml/min)

Sample	Heating Rate (°C/min)	Weight (mg)	Weight Loss (%)
A	10	6,384	92,37
B	25	4,524	86,32
C	50	5,168	85,02

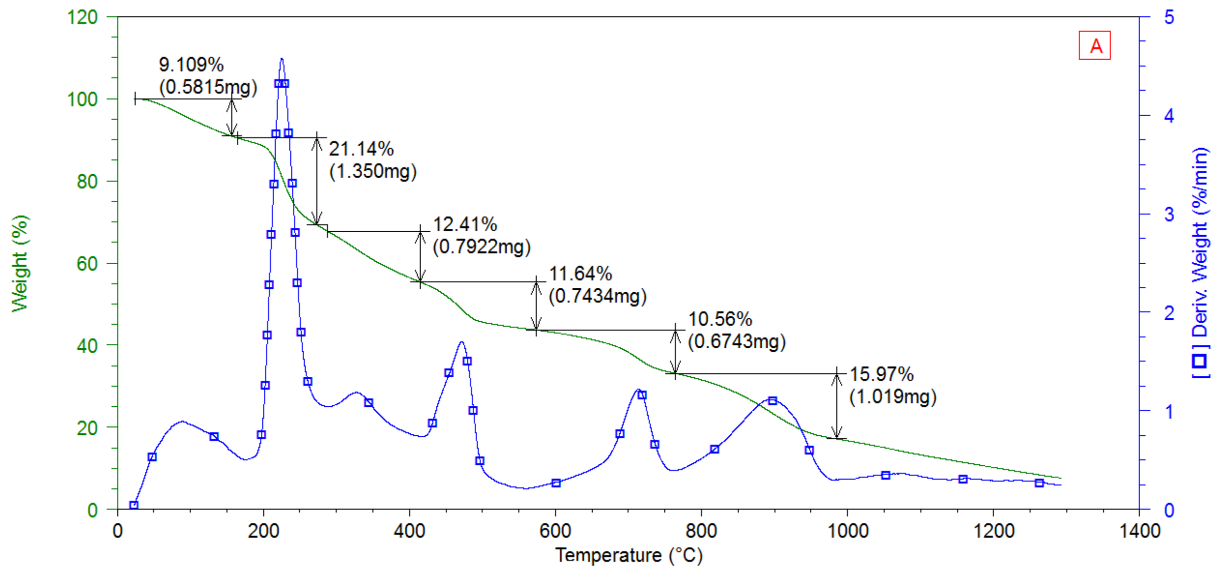

Fig 3. TG and DTG curves at heating rate of 10 °C/min for *Ulva lactuca*

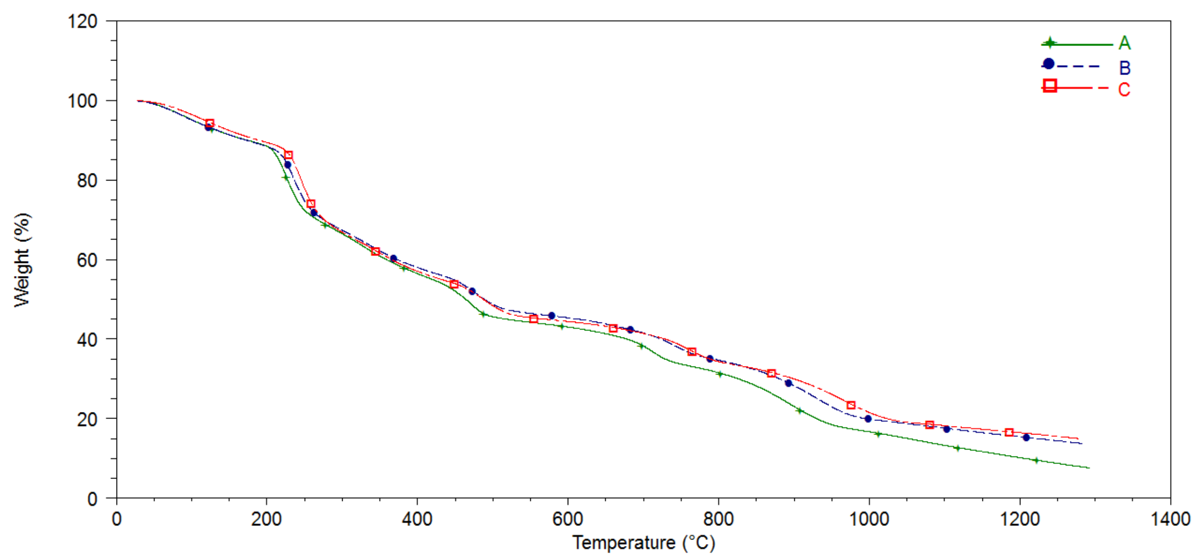

Fig 4. TG curves at heating rate of 10 (A), 25 (B) and 50 (C) °C/min

As it can be seen in the Figure 3, the TG curves of *Ulva lactuca* indicated that there were four basic stages in the thermal degradation and main decomposition step was occurred at lower temperatures. In the first stage (up to about 200°C), the weight loss was observed because of the loss of water (cellular and external water) from the sample. Main degradation was seen in the second stage over a temperature range of 200–600°C. The maximum rate of weight loss was observed around 225°C for *Ulva lactuca* due to the degradation of organic components (such as carbohydrates) and loss of volatile components [25], [27]. In this stage, the total weight loss is 45,19% (2,8856 mg). The third stage lies between temperatures of 600–750°C in which easily volatilizing inorganics are eliminated in addition to the decomposition of stabile organic polymers. In the last stage, the thermal decomposition continued until the final temperature. This resulted from thermal transformation and volatilization of the remaining inorganics in *Ulva lactuca* [23]. And also weight loss (%) of algae samples increased with increasing of heating rate values (Figure 4.).

Conclusions

Currently, utilization of macroalgae placed in the coastal areas as a waste is a promising way for both preventing pollution and producing valuable products such as bioethanol, biochar and activated carbon. Macroalgal wastes can be used as soil improver, adsorbent and energy source via carbonization process. In this article, carbonization of algae and algal wastes, effects that influence the product yields and some usage areas are mentioned briefly. An experimental study is also performed to investigate the productivity of algal biochar and TG analysis are performed for characterization of macroalgal biomass. It is concluded that macroalgal wastes have significant potential for waste utilization and biochar production.

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