Thermogravimetric characteristics and pyrolysis of red seaweed *Gracilaria gracilis* residues

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Abstract Algae are considered a future feedstock for biorefinery and also for 3rd generation biofuels. In this study the main objective was the investigation of pyrolysis characteristics of red seaweed residues by means of a thermogravimetric analyzer and a fast pyrolysis captive sample reactor. The red seaweed *Gracilaria gracilis* was collected in the Lesina Lagoon (Southern Adriatic Sea, Italy) where a stable coverage was found and algae were treated for phycobiliproteins extraction. The remaining algal biomass was pyrolysed for fuel and material production. Thermal degradation behavior of the macroalgae residue has been investigated using thermogravimetry (TGA). Pyrolysis was also studied at a range of 450-650 °C in a captive sample reactor. The yield of pyrolysis products (char, liquid) was quantified. The yield and composition of products from seaweed residues pyrolysis were compared with those obtained from agro-residues.

Keywords: macroalgae, TGA, pyrolysis, gas composition

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Introduction

Marine macroalgae is a potentially important source of renewable energy used for solar energy conversion and biofuel production. The average photosynthetic efficiency of such aquatic biomass is 6–8% [1] whereas the corresponding values for terrestrial biomass are between the range of 1.8–2.2% [2].

Macroalgae are classified in the following categories; a) blue algae (Cyanophyta), b) green algae (Chlorophyta), c) brown algae (Phaeophyta) and d) the red algae (Rhodophyta). Seaweeds are massively cultivated in the Far East; however only on a smaller scale in Europe. Seaweed aquaculture faces the challenge of growing fast rate macroalgae in the open ocean, reducing collection costs and avoiding environmental damage. Improving farming methods renders marine a potentially viable energy crop.

Towards this direction, inshore seaweed aquaculture is considered well established, while offshore is having more challenge [2].

Although algae have been studied intensively last years for biofuel production, commercial-scale production of biofuels using algal feedstocks is currently economically not viable. For both macro and microalgae, extracting other valuable chemicals is seen as a key way to increase revenue and reduce the net cost of fuel production. Seaweeds are the main resource materials for phytocolloids such as agar, carrageenan (derived from Rhodophyta) and alginates (derived from Phaeophyta) [3, 4]. Not only the algal biomass but also the residues from algal processing, in the context of a biorefinery, also represent a renewable source of energy (biorefinery residues and wastes). Algal residues can furthermore treated (gasified or pyrolysed) for further valorisation. In such a theromochemical algal waste sub-biorefinery, residues can be converted into biofuels and other bioproducts,

The topic of using algae biorefinery wastes for a post pyrolysis valorisation is new and therefore the studies reported are recent and few. Indeed, there is a shortage of research studies in the international literature on the post fermended or extracted algae residue [5-10].

There is also a shortage of bibliographic reference on seaweed characterization as fuels comparing also the composition of the marine biomass to conventional terrestrial biomass [2]. Few studies exist regarding thermochemical conversion of macroalgae via direct combustion, gasification, pyrolysis and liquefaction while the biochemical composition of different seaweed species have been studied in detail [11, 12]. Seasonal variations in biochemical composition and ash content have been also reported [13].

In this study the suitability of macroalgae residue for energy, fuel and biochar production is discussed in terms of thermochemical routes and specifically via pyrolysis. A comparison with the compositions of other lignocelulosic biomass materials such as energy crops and terrestrial biomass which is being used for biofuels production, is provides in order to assess algal and their biorefinery residues suitability for fuel and power production.

Materials and Methods

Materials preparation and characterization

The selected macroalgae that was used in the present study was *Gracilaria gracilis.* The red seaweed *Gracilaria gracilis* was collected in the Lesina Lagoon (Southern Adriatic Sea, Italy) where a stable coverage was found. The macroalgal biomass was initially dried in the harvesting facilities before being supplied to the lab for the experiments. The macroalgae (*Gracilaria gracilis)* was characterized and tested both as received, as

well as, after being subjected to phycobiliproteins extraction in the facility center of STAR agroenergy group in the University of Foggia in Italy.

The samples were ground to suitable particle size and sieved to powder of 1mm diameter. The elemental analysis of the samples was achieved with the method LECO-ASDM-D 5291. This method was accomplished with an elemental analyst CHN-LECO 800 and comprised by combustion in an oven. **Table 1** shows the elemental and **Table 2** proximate analysis of the macroalgae and the extracted residue, named as MA and R respectively.

Phycobiliprotein extraction

An amount of 0.5 g of freeze dried algal sample was ground manually with pestle and mortar. The mixture was suspended in 10 mL of 1 M acetic acid–sodium acetate buffer (pH 5.5) with 0.01% of sodium azide for 30 min in the dark. After the incubation with buffer, samples were ground for 5 min using a Potter homogeniser (Marconi, model MA099). The mixture was transferred in a centrifuge glass tube centrifuged at 5 °C, 15,000 g for 20 min. Supernatant was collected and pellet was extracted again with buffer as described for three times. Supernatants were combined and the final volume of the extract was about 40.0 mL. Phycobiliproteins (identified as R-phycoerythrin R-PE, phycocyanin PC and allophycocyanin APC) were quantified by spectrophotometry according to Kursar et al. [14]. The solid residue was dried in a oven (105 °C) overnight.

TG Analysis

Thermogravimetric analyses were performed at the Facility center of STAR Agroenergy in Foggia of Italy using a TGA analyzer unit (Mettler Toledo) under a flowing nitrogen atmosphere. Approximately 10 mg of sample was heated in a porcelain crucible up to 800 ºC at a rate of 10 ºC /min. Analyses were performed in duplicate.

Fast pyrolysis experimental procedure

The macroalgae (*Gracilaria Gracilis)* was tested both as received, as well as, after being subjected to phycobiliproteins extraction pretreatment process. Pyrolysis experiments were performed in the biomass group laboratory, of the Chemical Engineering department, Aristotle University of Thessaloniki, Greece.

Pyrolysis experiments were performed in a laboratory scale, wire mesh type reactor. The experimental apparatus comprised of two electrodes, an electrical circuit, a water cooling coil, a moisture trap, two filters for liquid hydrocarbons a helium providing

section, temperature controller and a gas sampling collection system. The produced pyrolysis' gas was analyzed offline in a gas chromatographer (Model 6890N, Agilent Technologies) fitted with two columns, HP-PlotQ and HP-Molsive type.The samples are weighted approximately 0.5gr and are placed in an envelope of stainless steel 100mesh. A thermocouple inside the sample, provides the temperature evolution and eventually the heating rate. The experiments are carried out at temperatures between 450-650oC, with a heating rate of approximately 50oC/s at atmospheric pressure and inert atmosphere.

Figure 1 shows the experimental set up. Pyrolysis experiments were carried out at three temperatures (630ºC, 750ºC and 850ºC).

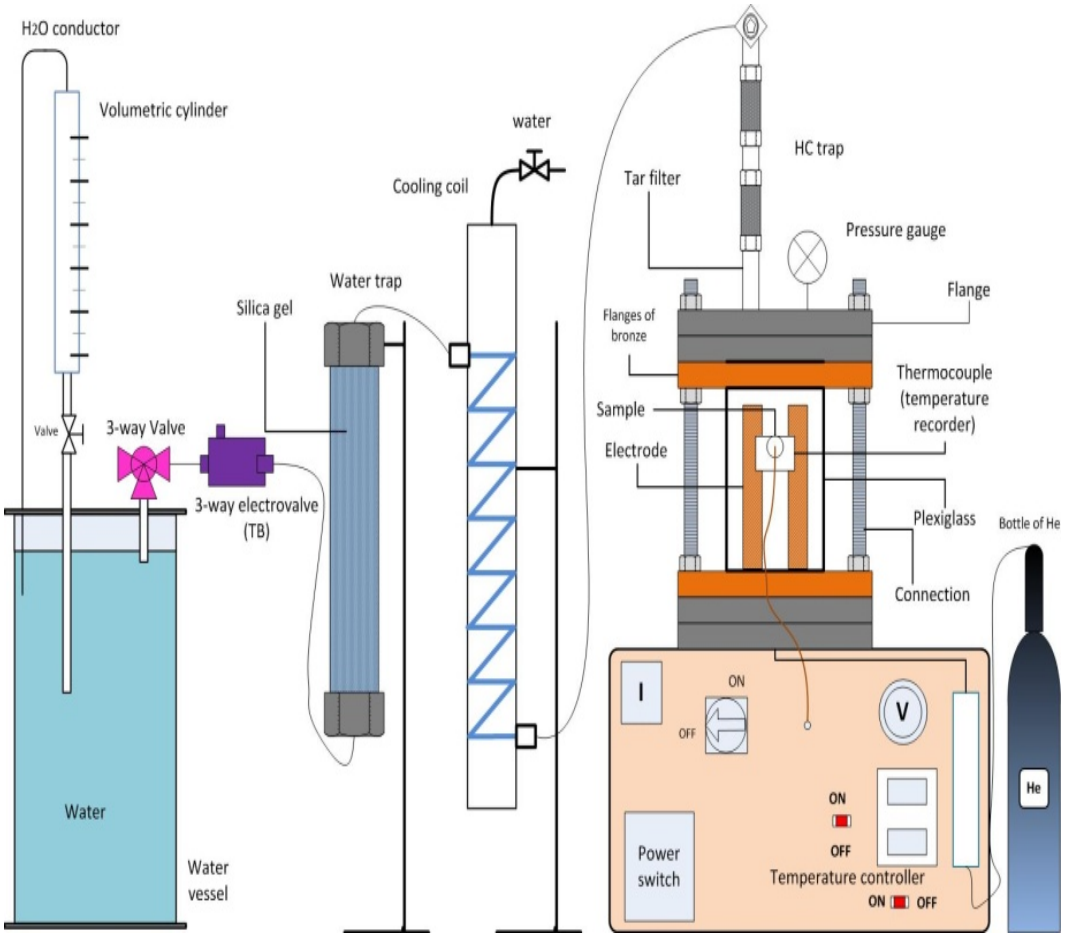

Figure 1 Experimental set up for fast pyrolysis. .

The reaction products include char, liquid and non-condensable gas. The char is remaining on the screen and after careful collection was determined gravimetrically. Tar was defined as the material condensed within the reactor vessel, on the wall, flanges and on a paper filter at the exit of the reactor, at ambient temperature. Tar also needed a very careful and complicated collection. Tar condensed within the reactor vessel, on the wall and flanges of the reactor and on the paper filter at the exit of the reactor. Tar was

condensed inside the reactor, removed by washing with C_3H_6O (acetone) soaked filter paper and measured gravimetrically. The liquid product was consisted by tar and liquid hydrocarbons. Hydrocarbons in the vapour phase at room temperature were collected in a lipophilic trap containing 80:100 mesh Porapaq Q chromatographic packing, placed at the exit of the reactor and then measured gravimetrically. It is evident that since the capacity of the reactor is very small and the collection of very small amounts of tar and char is difficult, any loss in collection has a very high impact on yields calculation and therefore on mass balance

Results and discussion

Macroalgae characteristics

Gracilaria Gracilis as well as the post phycolibiprotein extraction residue were characterized via proximate and ultimate analysis and the results are presented in **Table 1** and **2.**

Phycobiliproteins are proteins with linear tetrapyrrole prosthetic groups (bilins) that, in their functional state, are covalently linked to specific cysteine residues of the proteins. These proteins are found in cyanobacteria (blue-green algae), in a class of biflagellate unicellular eukaryotic algae (cryptomonads), and in Rhodophyta (red algae). In all of them the phycobiliproteins act as photosynthetic accessory pigments [15].

Table 1. Proximate analysis of Gracilaria Gracilis and Gracilaria residues as aby-product of phycobiliproteins extraction.

Sample	Moisture %	Volatile Dry %	Ash Dry %	Fixed Carb Dry %
Gracilaria Raw	9.13	67.32	19.98	12.70
Gracilaria Extracted	1.32	74.99	20.88	4.14

The residue after the extraction of high added value compounds as phycobiliproteins can be potentially further valorized via pyrolysis for liquid fuel and solid material production.

Table 2. Ultimate analysis of Gracilaria Gracilis and Gracilaria residues as a by-product of phycobiliproteins extraction.

	Carbon %	Hydrogen %	Nitrogen %	Sulfur %	Protein %
Gracilaria Raw	31.53	5.13	4.07	1.61	25.43
Gracilaria Extracted	31.67	5.17	3.98	1.58	24.88

Thermal degradation characteristics

The TG and DTG curves that were obtained from the pyrolysis of *Gracilaria gracilis* and the residue after phycobiliprotein extraction, at a heating rate of 10 °C/min, are depicted in **Fig. 1** and **2**.

Depolymerization of the particular macroalgae as well as of the residue after phycobiliprotein extraction processing takes place via is a complex mechanism and proceeds by several competing and concurrent reactions. During these reactions, cleavage of various bonds takes place in a wide range of temperatures based upon the bond energy. The obtained DTG curves show that the two samples undergo decomposition processes at different temperatures. The DTG peaks among the samples differ in position and height, implying a direct impact on thermal decomposition characteristics by the specific distribution of organic and inorganic constituent.

The different thermal degradation behaviour that the samples present (**Fig. 1, 2**) is attributed to the differences in the inherent structural and chemical characteristics of the samples that are related to the specific cellulose, hemicellulose and lignin content [16].

The thermal degradation onset temperature occurs at a lower temperature in comparison with terrestrial lignocellulosic biomass materials, as reported in literature [2, 17]; straws and grasses of high cellulosic content, woody biomass of high lignin content, different agro-residues and agri-food industrial solid residues as well as biomass pretreatment materials such as lignin and pulp. The behavior could be attributed to high carbohydrate and protein content as well as to the catalytic influence of the inherent metals

In general, regarding lignocellulosic biomass materials, the first decomposition regime represents the decomposition of hemicellulose and the second corresponds to the decomposition of cellulose. For the flat tailing section lignin is responsible, which is known to decompose slowly over a broader temperature range. Hemicellulose is the most reactive compound that decomposes between the range of 200 and 350 ºC [18, 19].

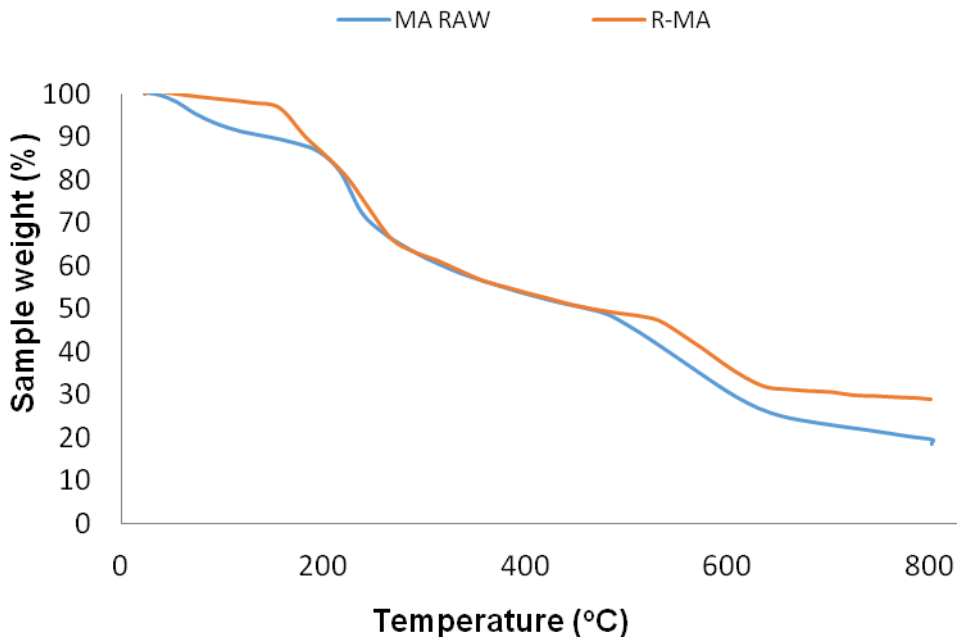

Fig. 1 TG pyrolysis profiles of Gracilaria gracilis residue after phycolibiprotein extraction (R-MA) and raw Gracilaria gracilis at a heating rate of 10°C/min (nitrogen atmosphere).

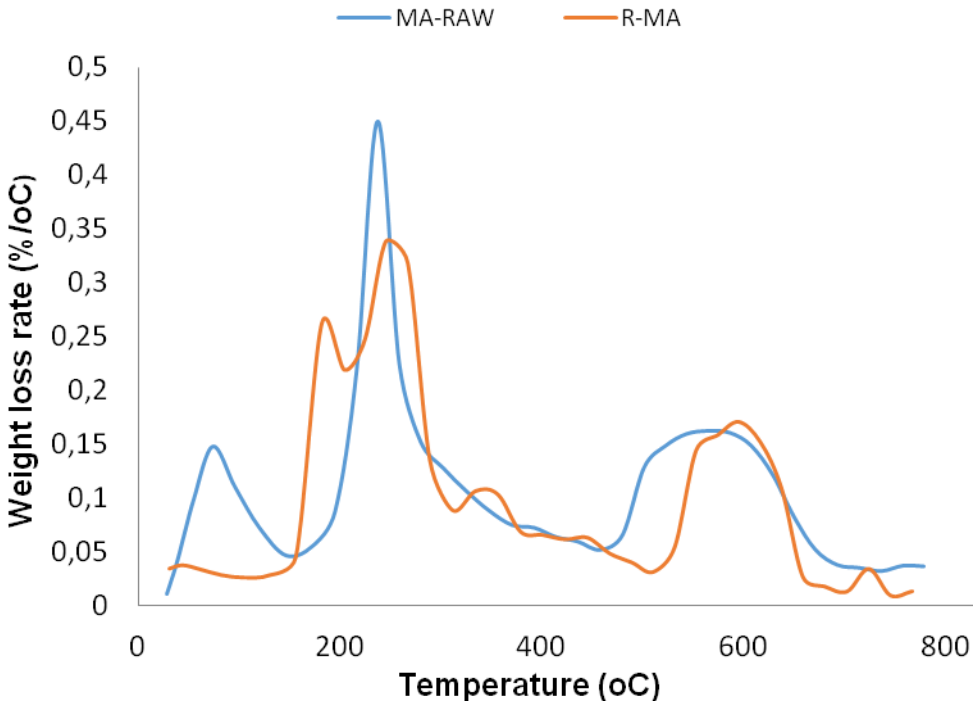

Fig. 2 DTG curves of Gracilaria gracilis residue after phycolibiprotein extraction (R-MA) and raw Gracilaria gracilis at a heating rate of 10°C/min (nitrogen atmosphere).

Relatively, regarding macroalgae mass loss between the range of 180– 270ºC is attributed to the decomposition of carbohydrate while the degradation of proteins takes place between 320–450ºC [2].

Regarding macroalgae residue after phycobiliprotein extraction, the main weight loss appears to be in the region of 250 ºC. DTGmax is shifted to the right comparing with the temperature (~230ºC) that major weight loss of raw macroalgae occurs.

Above 500ºC, the weight loss might be also attributed to carbonate decomposition [2].

Fast pyrolysis product yields

The char, liquid product yields as well as the total volatile release during fast pyrolysis of macroalgae residue, at three representative temperatures, are presented in **Fig. 3**. In the same figure the total volatiles release regarding fast pyrolysis of raw macroalgae in the same characteristic temperatures is provided for comparison.

Product yield distribution is a function of the feedstock and the temperature. At medium temperature (550oC) pyrolysis gives higher oil (reaching values of 70wt%) yields and lower char yields.

Macroalgae residue releases during fast pyrolysis experiments less amount of volatiles comparing with the raw material, which is attributed to the pretreatment process and the phycobiliprotein extraction.

Pyrolysis refers to the thermal decomposition of organic compounds under exclusion of air. The liquid product yield is dictated, firstly, by the composition of the feedstock [20] and, secondly, by the pyrolysis conditions

The influence of the pyrolysis temperature was likewise investigated by Demirbas. The optimum in terms of oil yield is at 500 °C [21]. Generally, pyrolysis oils are mostly highly viscous, acidic and unsaturated. They also contain solid matter as well as dissolved water. To enable the products to be used as regular fuels, their oxygen content must be lowered and the impeding substances removed. This can be done by means of hydrogenation processes for example [22].

Algae pyrolysis could give biooil, gas and a solid product called biochar. 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) [23].

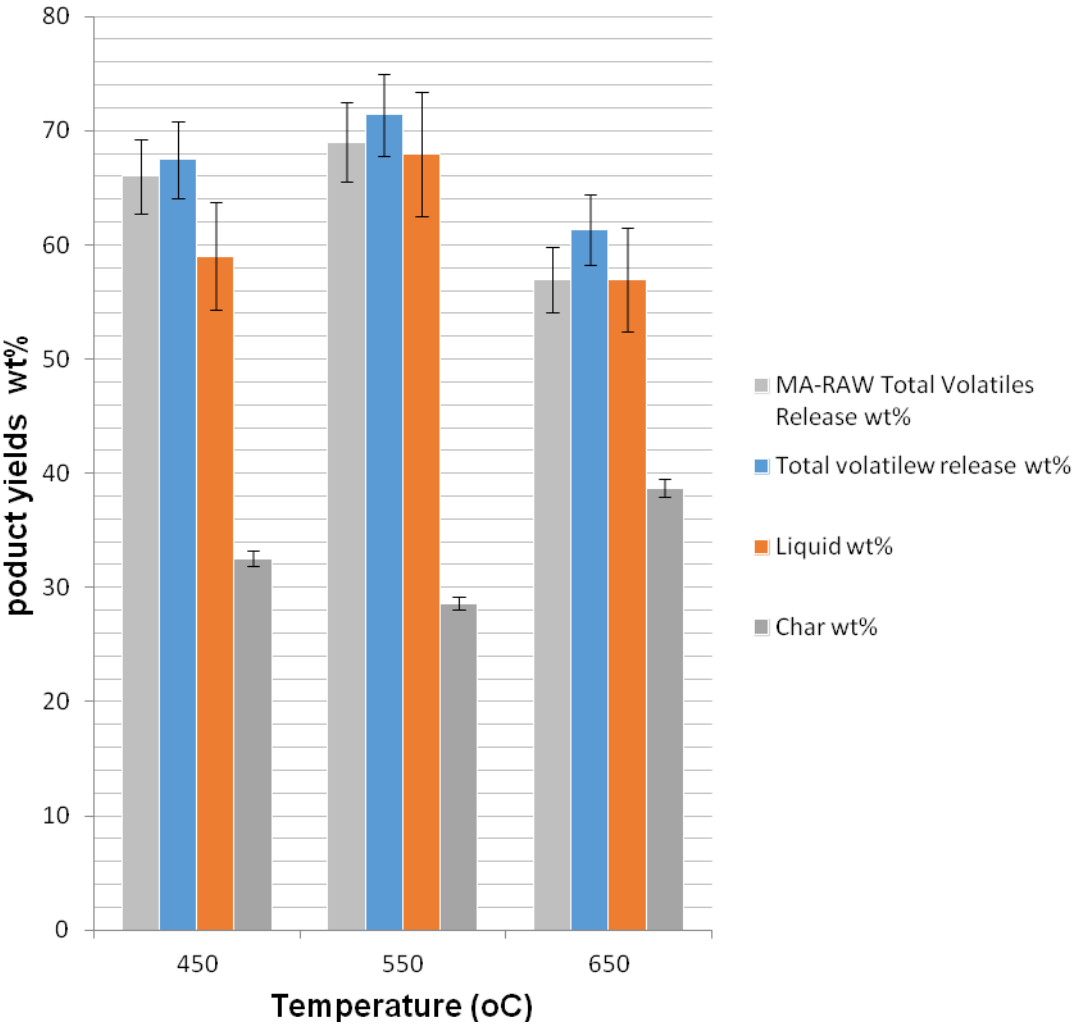

Fig. 3 Total volatiles release of macroalgae and the residue, as well as liquid and char yield results of the residue via fast pyrolysis at 450 ºC, 550 ºC and 650ºC.

Conclusions

Algae are considered a future feedstock for biorefinery and also for 3rd generation biofuels. The different thermal degradation behaviour that the is attributed to the differences in the inherent structural and chemical characteristics of the samples. Product yield distribution is a function of the feedstock and the temperature. At medium temperature (550oC) pyrolysis gives higher oil (reaching values of 70wt%) yields and lower char yields.

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