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Pyrolysis of different biomass: Direct comparison among Posidonia Oceanica, Lacustrine Alga and White-Pine

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HIGHLIGHTS

- Different kinds of biomass were selected to carry out pyrolysis experiments.
- The experiments were conducted in a fixed bed reactor at different temperatures.
- Bio-oil and bio-char characterization was carried out.
- The yield of bio-oil from pyrolysis process was evaluated.

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ABSTRACT

An investigation on the feasibility of producing bio-oil and bio-char fuels from wood chips (White-Pine), a Mediterranean seaweed (Posidonia Oceanica) and a local freshwater alga (Lacustrine Alga) by pyrolysis was carried out. Experiments were performed in a fixed bed reactor at different temperatures (400, 500 and 600 °C). Thermo-gravimetric analysis (TGA/DTG) were used in order to investigate the pyrolytic behavior. Product yields and composition from algal pyrolysis were compared with those obtained from terrestrial biomass.

Yields of char were in the range 22–48 wt% for algae and 20–27 wt% for lignocellulosic biomass. Due to the higher ash content (17–38%), the char obtained from algal biomasses had a lower heating value than that from White-Pine chips. By contrast, the oil yields from algae varied between 34 and 55 wt%, whereas yields from lignocellulosic biomass were in the range of 41.4–47.2%. The oil from Posidonia Oceanica showed a high heating value (HHV = 26.1 MJ/kg) close to the value of the oil obtained from White-Pine (30.1 MJ/kg). Chemical composition of liquid samples obtained at 500 °C was analyzed by GC–MS to identify organic functional groups.

1. Introduction

The worldwide interest on renewable energies, arising mainly from the environmental constraint, is greatly increased in the last decade. Among proposed alternatives, attention was recently addressed toward the employment of biomass and biofuels (biogas, ethanol, glycerol, organic waste, etc...) [1–5] as a feedstock for energy production through gasification technology sector and alternative way to the classic technologies used to separate and to fix CO_2 [6–9]. The uses of lignocellulosic biomasses are widely studied due to the low cost and high yield in products such as gas and bio-oil; however, the terrestrial biomass show often lower yields if compared with algal biomasses (both micro- and macroalgae) [10,11]. Algae, therefore are considered as among the most potentially significant future sources of sustainable biofuels, nevertheless despite their obvious potential, there are aspects that limit their use (i.e. the high water content and no commercial-scale quantities) [12–15].

Thermo-chemical processes such as pyrolysis, gasification and liquefaction are the most common techniques used for production of bio-fuels and bio-char. Pyrolysis needs lack of oxidant agent and moderated temperatures to produces pyro-gas, bio-oil and bio-char. These products can be used directly or after processing as fuel. Bio-char and bio-oil not only have applications as fuel but also can be used as a source for chemicals and value-added products [16].

Studies by Miao et al., reported the yield of bio-oil obtained by pyrolysis of Chlorella protothecoides of 54.9% at a temperature of 450 °C. The bio-oil obtained from algae is also characterized by a low content of oxygenated compounds, a high heating value (41 MJ/kg) and a low density (0.92 kg/l) [17,18].

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Bio-char is the solid product from pyrolysis and it can be used not only as a fuel but also as a carbon sink. Due to its molecular structure, it is quite stable both chemically and biologically, which means that it can remain stable in soil for 100 or even 1000 years [19,20]. The quality of activated carbon for its application strongly depends on the composition and structure of the precursor as well as type of activation process [21].

On the whole, current studies are mainly focused on determining the nature and characteristics of bio-oils and bio-chars for potential environmental and industrial applications, although still difficult to predict either the behavior or resulting features of a particular biomass species (mainly algal biomasses) subject to pyrolysis base upon available information in the literature. Hence, authors would report main results of an investigation on the effects of slow pyrolysis process apply to different "local" algal biomasses species. Detailed proprieties of bio-chars, bio-oils produced were compared to a woody material pyrolysis. In particular, algal biomasses examined regard: Posidonia Oceanica and a Lacustrine Alga (typical sea plant and freshwater alga of the Mediterranean area respectively), while white pine chips were used as woody biomass. Samples of three biomasses were previously investigated with the thermo-gravimetric analysis (TGA/DTG) for obtain the relationship between the weight loss and the temperature due to the decomposition, oxidation and dehydration and its derivative with the temperature. Successively, bio-chars and bio-oils samples were characterized by X-ray and gas-cromatography techniques.

2. Experimental section

2.1. Biomass preparation

Different kinds of biomass were selected to carry out pyrolysis experiments. In particular, a lignocellulosic material (White-Pine chips) has been compared with a sea plant (Posidonia Oceanica) and a freshwater alga (Lacustrine Alga). All feed-stocks were air-dried (at 110 °C for 1 h), shredded and sieved into a size range of 16–25 mesh. Prior to dry the algal biomass different washing with distilled water were carried out on both Posidonia Oceanica and Lacustrine Alga.

2.2. Analytical methods

Prediction of higher heating values was carried out from proximate and ultimate analyses and results are reported in Table 1.

Proximate analysis included measurement of moisture content, volatile matter, fixed carbon and ash. The moisture content measurement were performed on biomass samples, dried in a convection oven at 110 °C until constant weight was recorded. The volatile matter content was determined by measuring weight loss after heating biomass samples to 575 °C in an alumina crucible under N_2 atmosphere. The ash content was measured by heating samples at 575 ± 25 °C for 24 h to constant weight in a muffle furnace and the fixed carbon fraction was calculated by subtracting the percentages of volatile matter, moisture content and ash.

Table 1
Physico-chemical properties of the feed-stocks.

Materials	White-Pine	Posidonia Oceanica	Lacustrine alga
Proximate analysis (wt%)			
Moisture	7.6	10.7	5.2
V.M.	74.2	53.1	26.2
F.C.	17.4	19.2	30.6
Ash	0.8	17.0	38.0
Ultimate analysis (wt%)[a]			
C	45.46	31.31	19.49
H	5.32	3.33	2.41
N	0.18	1.08	2.43
S	0.05	0.14	0.23
O[b]	40.60	36.44	32.24
H/C atom ratio	0.12	0.11	0.12
O/C atom ratio	0.89	1.16	1.65
HHV (MJ/kg)	17.96	14.88	14.78
Protein (wt%)	–	6.75	15.18

[a] As received.
[b] By difference.

Elemental analysis was performed on both biomass samples and bio-char using Carlo Erba CHNS-O Elemental Analyzer. Based on the elemental composition and according to the literature [22,23], high heating values (HHV) of biomass and bio-oils were calculated.

Protein fraction was estimated based on the nitrogen content (wt%) of the biomass using a nitrogen factor (NF = 6.25) [24]. Protein fraction of all biomass samples was calculated as follows:

$$\text{Wt\% protein} = \text{N wt\%} * \text{NF} \tag{1}$$

2.3. Thermo-decomposition analysis

The thermo-decomposition of lignocellulosic matter and algae under pyrolysis have been investigated by thermo-gravimetric analysis (TGA) and derivative thermo-gravimetric (DTG) measurements. These techniques measure the amount and rate of change in the weight of material as a function of temperature. The temperature at the peak (the minimum or maximum) of the DTG curve represents the thermal decomposition of the samples. If the peak of the DTG occurs at a low temperature, the reaction can occur easily, and the height of the DTG curve identifies the capability to release volatile matter from a reaction during the pyrolysis process. The experiments were carried out by feeding the feedstock samples to a thermogravimetric analyser (Netzsch Thermische Analyse TASC 414/2). The tested conditions were controlled under a nitrogen atmosphere at a temperature from 25 to 900 °C with a heating rate of 10 °C min^{-1}. The TGA and DTG plots of all samples are shown in Fig. 1.

2.4. Pyrolysis measurements

In all experiments, about 1 g (16–25 mesh) of feedstock was fed into a stainless steel fixed-bed reactor with a height of 500 mm and a diameter of 6 mm. The experimental setup is shown in Fig. 2. Nitrogen gas was fed at a flow rate of 30 ml min^{-1} for 15 min. to remove the air in the reactor before testing. The tests were started by heating the reactor at a rate of 30 °C min^{-1} until the temperature reached a set temperature between 400 °C and 600 °C. Then, the reactor was kept at the constant temperature for 45 min. The gas leaving the reactor was condensed in three water-cooled condensers and was kept in liquid form (bio-oil); while the solid residue (bio-char) remained in the reactor. The pyrolysis product yields were calculated using the following equations:

$$Y_{\text{char}} = ((W_{\text{char}} - W_0 A)/W_0(1 - A - M)) * 100\% \tag{2}$$

$$Y_{\text{oil}} = (W_{\text{oil}}/W_0(1 - A - M)) * 100\% \tag{3}$$

$$Y_{\text{gas}} = (1 - Y_{\text{oil}} - Y_{\text{char}}) * 100\% \tag{4}$$

where W_{char} is the weight of char obtained during experiments, W_0 is the initial weight of the biomass, W_{oil} is the weight of oil obtained from experiments, A is the ash content, and M is the moisture content in the biomass (wt%, dry basis) [25].

2.5. Bio-oil and bio-char characterization

Bio-oils and aqueous samples were extracted with dichloromethane (1:1, v/v) and, extracts were qualitatively analyzed by