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Pyrolysis characteristics of a macroalgae solid waste generated by the industrial production of Agar–Agar

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ABSTRACT

A biomass solid waste (algae meal) generated by the industrial production of Agar–Agar was used as a pyrolysis precursor for this work. The optimal pyrolysis conditions for obtaining energy from the fractions generated (char, oil and gas), and for preparing adsorbent materials from the char were established. Chemical analysis of the algae meal showed that its high carbon, hydrogen and nitrogen content together with its low ash content make it a potential precursor of activated carbons. The optimal pyrolysis conditions were selected by means of thermogravimetric analysis and a study of the carbonization process of the algae meal. These conditions were: final temperature: 750 °C; heating rate: 5 °C/min, time at final temperature: 60 min; flow of inert gas (N_2): 150 ml/min. The char obtained from the pyrolysis process presents properties that make it suitable as a solid fuel and as a precursor of activated carbon. Analysis of the oil fraction by the chromatographic technique (GC–MS) showed compounds such as phenols, pyrroles and furanes. The gas fraction had a high syngas content enhancing its high heating value.

1. Introduction

The use of biomass as an energy source is becoming increasingly common, especially when it is obtained from agricultural, urban or industrial wastes. Party because it is considered to have a net zero CO_2 impact [1]. Among the various processes of biomass conversion, pyrolysis is a good way of waste processing, as it is able to process a wide variety of residues including municipal solid waste [2], plastic waste [3], agricultural residues [4], sludges [5], etc. The pyrolysis process is defined as the thermal decomposition of a material in the absence of oxygen or any other oxygen-containing reagent (air, water, carbon dioxide). As a result of this decomposition, a solid material (char), gas and condensable liquids fractions (oils) are obtained which in their turn can be used as fuel. Pyrolysis is seen as a highly versatile process that allows optimization of variables such as temperature, heating rate, annealing time, etc., depending on whether the aim is to maximize the char, oils, or gases yields [6–9]. Moreover, the solid material (char) can be used as a potential precursor of activated carbon.

The main objective of this paper is to determine the potential energetic uses of chars, and the condensable and gaseous products generated from the pyrolysis of marine biomass waste (solid waste originated in the industrial production of Agar–Agar from alga *Gelidium sesquipedale*). Moreover, their potential use as precursors for activated carbons of char obtained from waste algae pyrolysis will also be investigated.

The origin of the material used in this research work is called "seaweed meal" obtained from an industry located in northern Spain. This industry is one of the largest world producers of Agar–Agar, with a production of 2000–2400 kg/day of this waste. Currently, a portion of this residue is used for fodder and fertilizer although most of it is disposed off. For this reason a rational utilization of this waste is an interesting proposition.

Although many studies have been conducted on microalgae, little research has been focused on the use of macroalgae as a source of energy. However, there are no reports in the literature on the processing of residues from the industrial production of Agar–Agar. Ross et al. [10] evaluated the behavior of "*Brown algae*" when subjected to pyrolysis, using the TGA technique PY-GC/MS, before and after treatment with acid water. Yanik et al. [7] analyzed the pyrolysis yields of "*Laminaria digitata*" algae as well as different mixtures of algae from the Black sea. Bae et al. [11] studied the behavior of two types of brown seaweed *Laminaria japonica* and *Undaria pinnatifida*, and *Porphyra tenera* red seaweed during the pyrolysis, to determine the properties of the resulting bio-oil. Li et al. [12] studied the pyrolysis and the kinetic behavior of three types of algae: *Pophyra yezoensis*, *Harv and Corallina telfairiae*, *Plocamium pilulifera*. Chaiwong et al. [13] analyses the bio-oil and char fraction from algae by slow pyrolysis.

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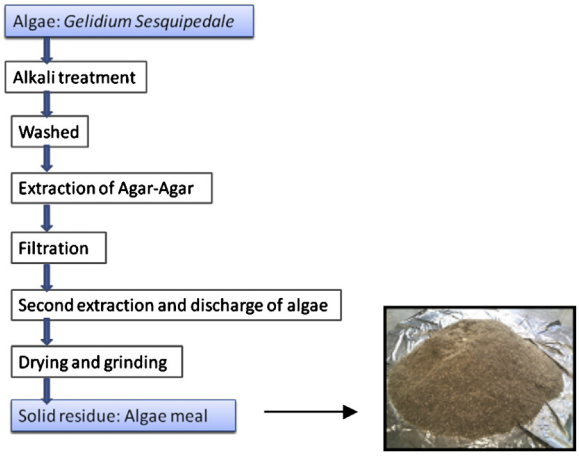

Fig. 1. The industrial process used to obtain Agar–Agar and the macroalgae residues.

2. Experimental

2.1. Biomass. Industrial process

Algae meal is generated from the industrial processing of macroalgae of the *Gelidium* variety, generally *Sesquipedale* to obtain Agar–Agar, which is a polysaccharide used to obtain a gelatinous product employed at the laboratory and culinary scale. The industrial process employed to obtain Agar–Agar and the resulting macroalgae residues is summarized in Fig. 1.

Once the seaweed is dried and packed in bales it is subjected to alkaline treatment with NaOH. Next, it is washed with cold water containing a bleaching agent. After this process, the seaweed is cooked and the Agar–Agar product is extracted, filtered and extracted again. After this second extraction, the obtained residue is dried and ground to obtain the precursor (algae meal) used in this work.

2.2. Experimental techniques

The algae meal was sampled by the plant for a period of one month. The material was quartered until a representative sample of about 2 kg was obtained. This sample was ground to <212 μm for chemical and thermogravimetric analysis. For the others experimental tasks the sample was used as received (Fig. 1).

2.2.1. Chemical characterization

The moisture content of the sample was obtained following the UNE 32002 norm, on the basis of weight loss at 105 °C over a period of 1 h and the ash content was determined by calcining the sample in a muffle at 815 °C for 1 h in the presence of oxygen, according to the UNE 32004. The carbon, hydrogen and nitrogen contents of the samples were determined using LECO CHN-2000 equipment. Determination of the sulphur content was carried out on a LECO S-144-DR equipment. The high heating value (HHV) was measured using an adiabatic IKA-calorimeter C4000.

The inorganic composition of the biomass (algae meal) was determined by ICP-MS and X-ray fluorescence (XRF). For the ICP-MS analysis the sample was dissolved in inorganic acids (HNO_3 4 N and concentrated HCl). Elemental analysis was carried out on an Agilent 7700x. For this purpose the sample was diluted and measured by the external calibration method between 0 and 1000 ppb internal standard (Sc). The beads for XRF analysis were prepared by fusing 6 g of lithium tetraborate for each 0.5 g of biomass ash sample (1000 °C) in a PHILIPS Model PERL X'3 automatic fusion bead machine. Elemental analysis was performed in standard conditions in a SIEMENS SRS 3000 XRFWD-XRF spectrometer fitted with an Rh target tube.

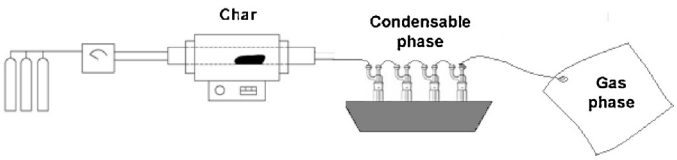

Fig. 2. Experimental set-up for pyrolysis in the electrical furnace.

2.2.2. Thermogravimetric analysis

The experiments were carried out on a TA Instruments thermobalance (TGA-Q5000IR). Pyrolysis was performed under a nitrogen atmosphere with a sample mass of approximately 10–20 mg, which was heated up to 1000 °C at a heating rate of 5, 10, 25, 50 °C/min. The experiments were performed under a carrier gas flow (N_2) of 90 ml/min in the sample.

A thermobalance SDTQ600 brand TA Instruments coupled to a mass spectrometer model Thermostar brand PFEIFFER VACUUM was used. Pyrolysis was performed under an argon atmosphere with a sample mass of approximately 10–20 mg, which was heated up to 1000 °C at a heating rate of 5 °C/min. Alumina capsules containing 90 μl of the sample were employed for this purpose. The gases released during the thermal process were analyzed in the mass spectrometer following multiple ion detection method (MID).

2.2.3. SEM-EDX

The algae meal and the char were examined using a scanning electron microscope (ZEISS Model DMS-942) equipped with an energy-dispersive X-ray analyzing system (Link-Isis II).

2.2.4. Pyrolysis process

The pyrolysis process provoked the thermal decomposition of the algae meal, as a result of which, three different products were obtained: a solid residue (char), a fraction of the condensable volatile matter (bio-oils and water) and a gaseous fraction (bio-gas).

The experimental set-up employed for the carbonization of the material, included a horizontal tubular furnace (Carbolite CTF 12/65/550), a mass flow controller (N_2 or Ar) and a series of cooling condensers for capturing the condensable phase and Tedlar sample bags for retaining gaseous phase (Fig. 2). For each experiments, approximately 20–30 g of algae meal was introduced into a small alumina annealed vessel which was placed in a quartz reactor.

The carbonaceous residue and the condensable fraction (bio-oil and water) were weighed in order to calculate the yields. The non-condensable fraction (bio-gas) were collected in 5–12 L capacity Tedlar sample bags and the gas yield was evaluated by difference.

2.2.5. Chromatographic analysis

The chromatographic analysis of the oil fraction was carried out on an Agilent 7890A chromatograph equipped with an Agilent-MS 5975C mass spectrometer. Separation was conducted on a HP-DMS capillary column (5% phenyl-methylpolysiloxane) (30 mm 0.25 mm ID × 0.25 μm), at an initial temperature of 50 °C which was maintained for 10 min up to the final temperature. 0.3 μl (splitless) of the sample was injected into the equipment. The peaks were identified by comparison with NIST08, Wiley 7n and Wiley 275 library data. Prior to analysis, the water of the condensable fraction was separated from the organic fraction by decantation. The organic fraction was dissolved in dichloromethane and the solution was dried, using anhydrous sodium sulphate and then filtered. The filtered solution was evaporated at room temperature during 24 h and then analyzed by GC–MS.