Macroalgae waste from the Agar-Agar industry: Bioenergy through pyrolysis processes (biofuels) and biogas upgrading

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Introduction

Marine macroalgae are commonly found at coastal regions, being transported from the water environment to the beaches. Such biomass remains in the beach areas (e.g. sand), being accumulated as solid waste and thus potentially affecting the environment and human health (Pardilhó, S.L et. Al.,2021).

This research is to focus on a solution for ensuring an effective management of a solid waste of the macroalgae "*Gelidium sesquipedale*" (algae meal, AM) resulting from the production of agar-agar, supply by the Roko S.A. industry which is located in Asturias (Northern Spain). Agar-agar production generates approximately 2000-2400 Kg/day macroalgae waste (AM), and their main use is as fertilizer and fodder for farms or in the worst case, its disposal in landfills (Ferrera-Lorenzo et al., 2014a). **Figure 1** shows SEM photomicrograph of AM at 500x magnification.

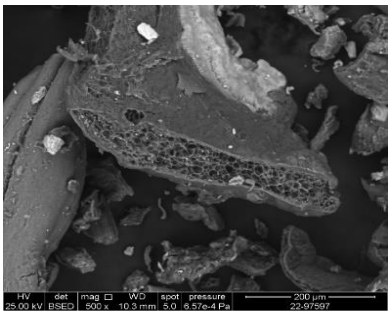

***Figure 1**. SEM macroalgae waste (AM)*

Traditionally, the use of biomass solid waste has been recycling-reuse or energy recovery through processes such as combustion, pyrolysis and gasification. An alternative is to obtain materials with high added value such as carbonaceous adsorbent materials, activated carbons (ACs).

The ACs are the adsorbents more widely used because its highly porous nature with tunable pore size and a large surface area. It is well-known among the applications for the treatment of gaseous emissions, ACs are used in the elimination of corrosive and toxic compounds, such as, acid gases (H_2S, SO_2 and NOx), they are also used in the capture of greenhouse gases such as CO_2 and CH_4, in the renewable energy industry to improve biogas by removing pollutants (CO_2, H_2S, VOCs such as siloxanes, etc.) (Saadi, W.,2021).

The aim of this work is to use an industrial macroalgae biowaste as a possible source of energy through conventional and flash pyrolysis to obtain bio-char, bio-oil and gas and to evaluate is potential in the bioenergy sector. Moreover, to evaluate the possibility to obtain sustainable ACs from macroalgae waste pyrolyzed (bio-char) by chemical activation using alkaline activating agent. These ACs will be evaluated as an alternative method for the purification/separation of gas mixture (CO_2/CH_4 or CO_2/H_2) with the biogas upgrading purposes for the renewable energy production.

Methodology

The industrial process for obtaining agar-agar from red macroalgae "Gelidium *sesquipedale*", where the macroalgae wastes are generated, it is described in Ferrera-Lorenzo et al. (2014a). Due to the industrial origin of the waste, it is necessary to collect and prepare it adequately and obtain a representative sample (≈1 kg to <1mm) by grinding and dividing.

The energy use of the macroalgae waste was carried out with different pyrolysis technologies (conventional and flash pyrolysis) using an electric, cylindrical and horizontal oven of original design. In conventional pyrolysis (PC), the sample was introduced into the oven at room temperature; employing nitrogen gas flow of 100 ml/min to inert the interior atmosphere of the reactor, the furnace programming set-up used a heating ramp of 25°C/min, pyrolysis temperature of 750°C or 850°C, the sample were held for 1 hour at the final pyrolysis temperature. In

flash pyrolysis (PF), the sample was instantly introduced into the oven when it reached working temperature (750 °C or 850 °C), after the pyrolysis process, three fractions were obtained (Bio-char, Bio-oil and gas).

Activated carbons were obtaining from the macroalgae waste pyrolyzed (bio-char) by chemical activation using alkaline activating agent (KOH and K_2CO_3) at different proportion (0,5:1 and 1:1). KOH-activated carbons were obtained at 700 and 800 °C and the K_2CO_3-activated carbons at higher activation temperature (850 and 950 °C) The ACs obtained from this macroalgae waste were prepared in a Carbolite CTF 12/65/550 horizontal electrical furnace. Finally, these carbonaceous adsorbents were used in studies of high-pressure gas adsorption (CO_2 up to 3 MPa, H_2 up to 4 MPa and CH_4 up to 8 MPa) at room temperature and under static conditions.

All the materials (macroalgae waste, bio-char, bio-fuel, gas and activated carbons) were characterized by different chemical, morphological, structural and textural analysis techniques.

Results

Ultimate analysis of macroalgae waste and the bio-chars was carried out, **Table 1.** The chemical analysis showed high carbon content and moderate nitrogen content; the bio-waste has a low ash content (10.6%) which increase to 30% in the bio-chars, Table 1, however the KOH-activated carbons present low ash content (<6%).

Table 1 *Chemical composition of biomass waste and bio-chars*

Sample	Ash (%)[a]	C (%)[a]	H (%)[a]	N (%)[a]	S (%)[a]	O (%)[a,b]	HHV (MJ/Kg)
AM	10.58	43.15	5.43	4.27	1.06	44.81	14.60
AMPC 750	26.32	62.66	1	4.3	1.7	27.84	18.00
AMPF 750	30.44	62.18	1.09	4.28	1.89	30.56	17.49
AMPF 850	30.13	62.66	0.85	4.14	1.99	30.36	17.35

[a] Dry basis.
[b] determinates by difference

The ACs obtained have a good chemical characteristic like a high carbon content, moderate nitrogen, and low ash contents; likewise, they present a good textural development show BET specific surface area higher than 1000 m^2/g, and high total pore volume. The adsorbent materials obtained in this work are mainly microporous. Chemical activation has different effects on the porosity development of the materials obtained. An increase in the activation temperature (850–950 °C) favored adsorbent materials with greater textural development.

ACs observe high capacity retention of CO_2 and CH_4, due to the good chemical and textural properties. The amount of CH_4 adsorbed is positively correlated with S_{BET}, V_{TOT}. These materials had negligible H_2 adsorption capacity which makes them useful for separating gas mixtures in order to obtain pure H_2.

Conclusions

In the yield of bio-char, bio-oil and gas obtained in PF, the gas yield at higher temperature was the highest (60%). HHV of gases derived from PF is of the order of three times higher than those from PC (16 MJ/kg) mainly due to the increase in the amount of CH_4 and H_2. Bio-char proven to be an effective material as precursors of sustainable porous carbon material (ACSs). ACs are microporous materials with a S_{BET} surface area are higher than 1100 m^2/g. Chemical and textural properties of the ACs obtained make them an excellent candidate for biogas upgrading.

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