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French Brittany macroalgae screening: Composition and methane potential for potential alternative sources of energy and products

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HIGHLIGHTS

- *P. palmata, G. verrucosa, U. lactuca* and *U. pinnatifida* are attractive for human consumption.
- The biochemical composition of *P. palmata* is favorable for anaerobic digestion.
- The best algae for alginate extraction are *S. polyschides* and *S. latissima.*

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ABSTRACT

Macroalgae are biomass resources that represent a valuable feedstock to be used entirely for human consumption or for food additives after some extractions (mainly colloids) and/or for energy production. In order to better develop the algal sector, it is important to determine the capacity of macroalgae to produce these added-values molecules for food and/or for energy industries on the basis of their biochemical characteristics. In this study, ten macroalgae obtained from French Brittany coasts (France) were selected. The global biochemical composition (proteins, lipids, carbohydrates, fibers), the presence and characteristics of added-values molecules (alginates, polyphenols) and the biochemical methane potential of these algae were determined. Regarding its biochemical composition, *Palmaria palmata* is interesting for food (rich in nutrients) and for anaerobic digestion (0.279 LCH_4/gVS). *Saccharina latissima* could be used for alginate extraction (242 g/kgTS, ratio between mannuronic and guluronic acid M/G = 1.4) and *Sargassum muticum* for polyphenol extraction (19.8 g/kgTS).

1. Introduction

Macroalgae are vegetables that are much less known than ground plants, and their growth is much more difficult to predict. They are not gathered in a homogeneous group but are divided into several lineages completely independent from one another. Thus, considering marine algae, there are essentially three types: brown, red and green seaweeds. There are, despite the similarities in shape, more genetic differences between brown algae as Fucus (seaweed from shore) and a green alga *Ulva* (sea lettuce) (Cabioch and Le Toquin, 2006) than between the latter and an oak. Some references provide an excellent overview of the seaweed resources and worldwide markets (McHugh, 2003; Wei et al., 2013). Seaweed could be used entirely or after some extractions in food industry and/or for energy production (MacArtain et al., 2007; Langlois et al., 2012).

Seaweeds are used as sea vegetables and highly consumed in Asian countries like China, Japan and Korea. Seaweed as vegetables is yet still not popular in French gastronomy but there is an increasing demand for these natural and healthy sea vegetables among consumers. Therefore in France, the supply of fresh seaweeds is not sufficient for the small industries which elaborate food products containing seaweeds. They need to import edible seaweeds from other countries.

Seaweeds are often used as feedstock for hydrocolloid production such as alginates, carraghenans and agar–agar (Bixler and Porse, 2010). Alginates, extracted from brown algae are constituted by the mannuronic (M) and guluronic acids (G). They are used as thickeners, gelling agents, emulsifiers and stabilizers of industrial products ranging from frozen food, cosmetics, even pictures and printing ink.

In Europe the main harvesters are Norway and France. Around 120,000 tons of *Laminaria* spp. are harvested annually in Norway. France harvests about 50,000–70,000 tons annually, mainly *Laminaria* species for hydrocolloid production.

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Macroalgae have been used for a long time in agriculture especially as a fertilizer such as wrack. The high fiber content of seaweed acts as a soil conditioner and assists moisture retention while mineral content is a useful fertilizer and source of trace elements. The development of organic farming favors the use of algae but not yet on a large scale (McHugh, 2003). Seaweed in agriculture could also be used in various forms such as biochars extracts or as biostimulants for plant growth. For example, some studies revealed that seaweed could be used to reduce fungal root infection and nematode's attacks in roots of a pathogen of tomato and sunflower (Sultana et al., 2011).

The worldwide increasing demand for energy coupled with the depletion of fossil fuel ressources implies the development of bioenergy and biofuel production. Thus, macroalga is an attractive source of biomass energy since they do not compete with land use and water consumption necessary for food crops production. Research in this field began in the eighties, while energy cost was very high (Chynoweth et al., 1987; Morand et al., 1991). Among macroalgae, the *Laminaria* spp. and *Ulva* spp. are the most investigated for an energy perspective. The energy development is usually envisaged as bioenergy, i.e. bioethanol and biogas production (Wei et al., 2013). Alcoholic fermentation is difficult because of the lack of easily fermentable sugar polymers such as starch, glucose or sucrose. In comparison to bioethanol production, anaerobic digestion of macroalgae represents the closest technology to commercialization since even complex carbohydrates can be transformed into biogas. Anaerobic digestion has also the advantage to be modular. Indeed, this technology represents a good way to produce energy (heat and electricity via cogeneration) from either the entire seaweeds or the co-products of the alginates or phenols extraction.

A recent life cycle analysis study was performed in order to assess if aquacultivated seaweeds could be considered as an environmentally friendly source of biomass for bioenergy (Langlois et al., 2012). They showed that the methane production from anaerobic digestion of the whole seaweeds or their residues after alginates extraction is more interesting from an environmental point of view than the exploitation of natural gas.

The study of the biochemical composition of algae would enable to optimize the identification of the best valorization ways (specific products for food industry, energy production i.e. biomethane). Marine algae consist of polysaccharides with no lignin and low cellulose content (Morand et al., 1991). The biochemical composition of macroalgae in terms of fiber, mineral content, lipids, and carbohydrates depends on the species and the season (MacArtain et al., 2007). Their composition differs from the red, brown or green seaweeds (Rinaudo, 2007).

The macroalgae investigated in this study were selected according to their natural presence on the French Brittany coast, to their ability to be cultivated and their potential valorization as food additives (Draget et al., 2005) and/or energy (Wei et al., 2013). The Channel coasts and in particular the North coast of Brittany have one of the largest seaweed production in Europe due to conditions such as the existence of a rocky foreshore linked to a wide tidal range, transparency and fertility of water, and their renewal by tidal currents and by the stirring of the medium. In this study, global valorization of seaweeds into energy and high added value products is considered. Therefore, a vast and deep characterization was performed on red, brown and green macroalgae, naturally present or cultivated in Brittany coasts (France). The characterization consists in determining the biochemical composition: minerals, fibers, proteins, lipids, carbohydrates (total and individual composition), polyphenols, salts, and to compare it to their biochemical methane potential to understand the eventual problems of degradability within the anaerobic digestion process. The aim of this advanced characterization is to propose, depending on the algae, and its biochemical properties the best way to put it to advantage (energy, food, food industry, etc.).

2. Methods

2.1. Marine algae

Brown seaweeds (*Undaria pinnatifida* (Up), *Saccorhiza polyschides* (Sp), *Sargassum muticum* (Sm), *Saccharina latissima* (Sl), *Himanthalia elongata* (He)), red seaweeds (*Gracilaria verrucosa* (Gv), *Palmaria palmata* (Pp), *Asparagopsis armata* (Aa)) and green seaweeds (*Codium tomentosum* (Ct), *Ulva lactuca* (Ul)), were collected in July 2010 at Lézardrieux (Côtes d'Armor. Brittany, France) by Aleor. The algae were washed with seawater, dried at 40 °C for 24 h and roughly chopped ($\approx 2 \times 2$ cm).

The seasonal variability for *S. latissima* was studied. Samples were collected each month during a 4-month period in 2011 from May to August.

2.2. Analytical methods

Most of the analytical methods are described by Jard et al. (2012), additional methods are explained in the following paragraph.

Total solids (TS) and volatile solids (VS) were determined on dry macroalgae according to standard APHA methods by drying the biomass at 105 °C (24 h) followed by incineration at 550 °C (2 h).

Total organic carbon was determined according to the standard method using a Shimadzu TOC-V analyzer. Total organic carbon was obtained after total combustion at 680 °C with a cobalt/platinum catalyzer in the presence of oxygen. Inorganic carbon was also measured but was near to zero therefore total carbon was assimilated to total organic carbon.

Measurement of total Kjeldahl nitrogen (TKN) was carried out using the normalized APHA method. The conversion factor 4.92 was used to estimate the protein content ($N \times 4.92$).

Lipid content was determined using the protocol described in the Commission Regulation (EC) No. 152/2009 (process B).

Sugar and mannitol contents were determined by reverse HPLC using Absorbosphere RP18 column (5 µm, 4×250 mm) after methanolysis. Total sugar content represents the sum of each sugar analyzed.

The ratio mannuronic acid/guluronic acid was performed by ^{1}H NMR analysis of sodium ailginate spectrum as previously described (Heyraud et al., 1996).

Total fibers were measured by an enzymatic-gravimetric method according to Lahaye (1991). The determination of soluble and insoluble dietary fiber from marine algae consists in gelatinization with Termamyl. Proteolysis and amylolysis were performed before extraction with ethanol. The residues were insoluble dietary fibers.

Analysis of minerals was performed by inductively coupled plasma-optical emission spectroscopy (Larrea-Marín et al., 2010). Sulfur analysis was analysed by elementary analysis using (LECO C ans S analyser).

Sulphate content was determined using a modified method based on Craigie et al. (1984).

Total phenolic compounds were determinated colorimetrically using Folin–Ciocalteu assay method according to Ragan and Glombitza (1986). Phloroglucinol was used as a standard.

2.3. Biochemical methane potentials

The biochemical methane potentials (BMP) were measured as described by Jard et al. (2012). Samples were prepared in triplicate in 500 mL plasma bottles. Each bottle contained 2 gVS of inoculum and 1 gVS of ground seaweed. Bottles were filled to 400 mL with a bicarbonate buffer complemented with nutrients (Supplementary