Available online www.jsaer.com

Journal of Scientific and Engineering Research, 2024, 11(3):238-247

Research Article

ISSN: 2394-2630
CODEN(USA): JSERBR

Valorization of Macroalgae Waste through the Production of Biomethane

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Abstract The coasts of the Atlantic Ocean are suffering from massive strandings of algae. These algae deposits cause significant health, socio-economic and ecological problems. In order to find a viable solution to manage and eliminate this environmental issue, this research work studied and proposed macro-algae methanization

The results showed that despite, a C/N ratio of 14.92 ± 0.78 and under ambient temperature and pressure conditions; the treatment of this marine waste by anaerobic digestion led to the production of biogas rich in methane (more than 60%) or a methanogenic potential of 0.787 LCH4/kgVS at a temperature of 28°C. the substrate studied also had 52.20 ± 1.18% dry matter and an average organic matter concentration value of 40% relative to its dry content. The qualitative and quantitative analysis of biogas production showed that to ensure continuous operation with flammable gas production, it is essential to take into account when designing the valorization unit through the methanization of stranded algae, that this marine biomass has a latency time of 30 days plus a residence time of 90 days under conditions which respect the sixth principle of green chemistry.

Keywords Macroalgae, Sargassum, Waste, Anaerobic digestion, Biogas

Introduction

Since the second half of 2011, the coasts of the Caribbean islands, the Gulf of Mexico, the southeast of the United States and the coasts of the Gulf of Guinea, namely Benin, Côte d'Ivoire, Ghana, Guinea, Liberia, Nigeria, Senegal, Sierra Leone and Togo are victims of massive algae strandings. These overabundant algae are primarily brownish algae and are technically called Pelagic Sargassum [1, 2].

Remaining sargassum deposits on the shore or in the immediate vicinity have significant negative impacts on aquatic resources, fisheries, waterways and tourism. In this regard, studies reveal proven nuisances, caused both by physical obstacles represented by slicks blocked in bays or washed up on beaches and by the chemical decomposition of wet sargassum, on land or in the water, which releases gases, notably hydrogen sulphide (H_2S). Hence, the consequences of these strandings of invasive species of algae on the shores are of significant health, socio-economic and ecological importance [2, 3]

In response to this environmental challenge, West Africa set up a technical working group [1]. However, to date, in Senegal, more precisely in the commune of Joal-Fadiouth, no effective solution has been found or implemented to combat beach pollution by sargassum

While at the same time others around the world are putting costly efforts into collecting and moving sargassum in time for it to decompose elsewhere. This unused biomass in the commune of Joal-Fadiouth could serve as raw material for biogas.

The population of Joal-Fadiouth lives mainly from fishing and tourism. And the municipality is typical for its energy dependence on fuel in their process of processing fish products. These characteristics make it a territory where the simultaneous production of biofuel methane and the elimination of unwanted biomass in a synergistic waste management system is a concept with environmental and resource conservation advantages [4]

It is in this spirit of proposing a viable solution for the management and elimination of massive flows of algae which flood the coasts of the Atlantic Ocean, particularly in the commune of Joal that we propose to experimentally study the methanization of sargassum under ambient temperature and pressure conditions. And the latter fits perfectly into one of the principles of green chemistry: "energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible synthetic methods should be conducted at ambient temperature and pressure" [5]

Methanization is a process carried out in a hermetic environment, the digester or reactor, in which many parameters, such as temperature, pH, and physicochemical properties of the input used, will influence digestion [6, 7].

So, in this study, we will carry out a physico-chemical characterization and an anaerobic digestion of the algae washed up on the coast of Joal-Fadiouth in order to carry out a qualitative and quantitative study of the biogas resulting from the methanization of these algae.

Such study contributes in the diversification of substrate in waste to energy project but also propose a solution in waste management.

Materials and methods

Presentation of the substrate

The algae washed up on the beach of the commune of Joal-Fadiouth ***(Figure 1)***, the first fishing wharf in Senegal in terms of landings, are the subject of this work. They are collected manually on May 4, 2022.

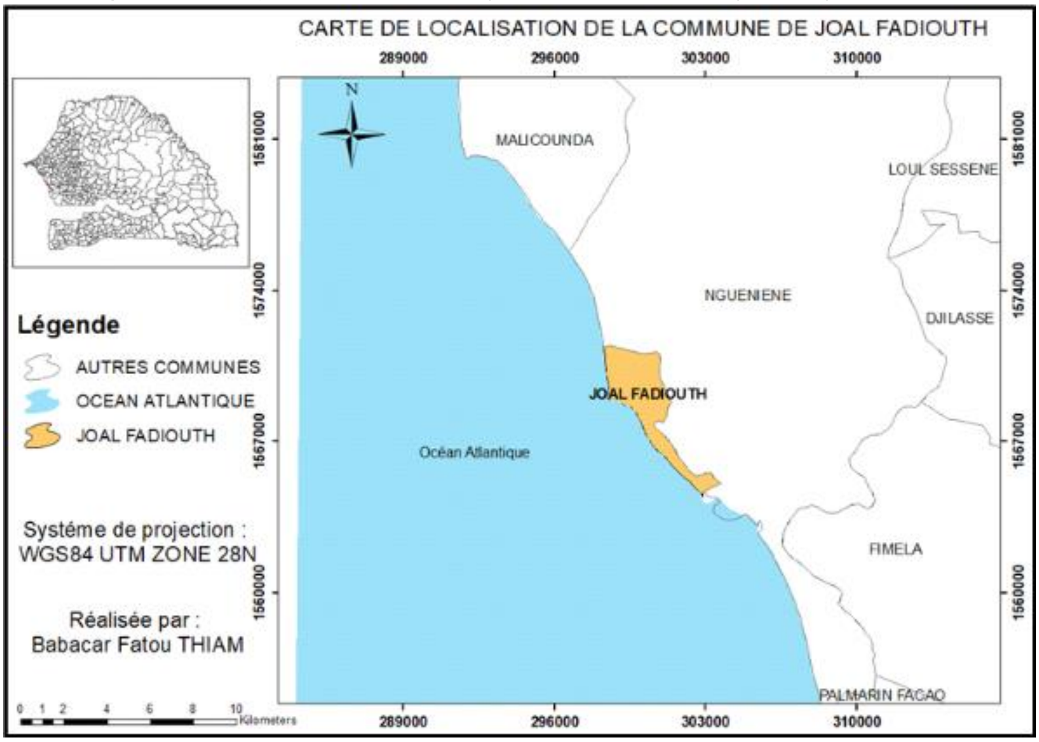

Figure 1: Location map of the commune of Joal-Fadiouth

The species in question are essentially sargassum, *Sargassum natans and Sargassum fluitans* are two species of pelagic brown macro-algae found in the Atlantic Ocean. Very similar, they differ mainly by the morphology of their leaves and the presence or absence of spiny structures.

The sargassum collected served as a sample for physicochemical characterization and as a substrate for studying the anaerobic digestion of stranded algae. Before carrying out these various tests, the effluent is washed to remove sand and salt from the sea water and allowed to dry in the shade before being crushed by a food grade multifunction grinder ***(Figure 2).***

Figure 2: Multifunctional grinder. A. grinder different parts. B. grinder assembled

This phase, washing and grinding, popularly called pretreatment ***(see Figure 3)*** is carried out, on the one hand to homogenize the raw material and facilitate handling for characterization tests and on the other hand to increase the surface area ratio. /particle volume to reduce the time required for hydrolysis of the substrate during conversion to biogas [8].

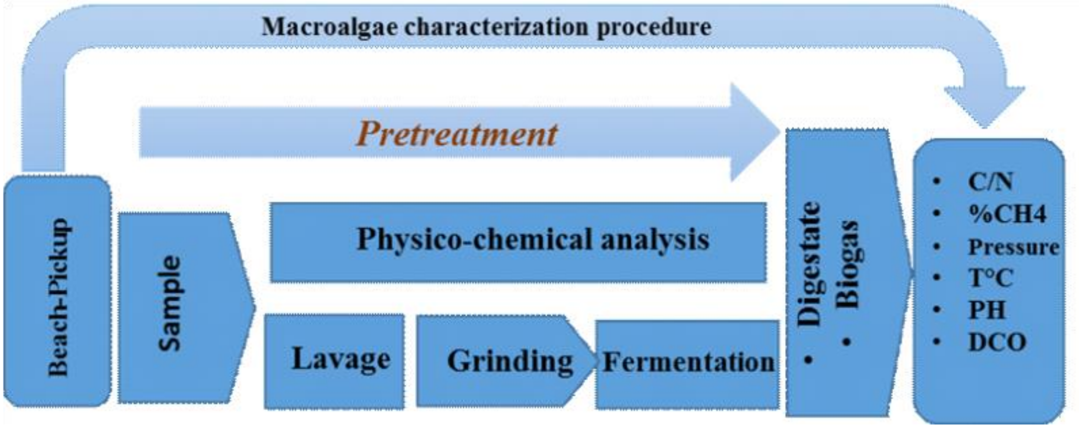

Figure 3: General study procedure

Physico-chemical characterization

The physicochemical characterization was carried out in the laboratory of sanitation of the Ecole Polytechnique de Thiès. It consisted of determining the dry matter, the moisture content, the Total Organic Carbon, and the Total Organic Nitrogen contained in the study sample. The methods used for testing and evaluating all of these intrinsic parameters of the sample are quite well known and described by most characterization articles [9, 10, 11, 12]. It is also the same processes and the same devices adopted and described by Fatou et al. in their study of biogas production by the Co-digestion of fish waste and casuarina litter as well as Ahmed Ahmedou El Hacen and Alassane Diène in the publication entitled Energy recovery from household solid waste from the city of Thiès: Characterization and production methane from food waste [13, 14].

All analyzes and tests were carried out three times and the results are presented as mean ± standard deviation.

Production device and monitoring of methanization

In order to study the complete digestion of organic materials, the fermentation takes place in a single bioreactor ***(see Figure 4).***

We designed our own reactor from 10 L transparent plastic mineral water bottles Figure 4. To ensure the sealing of our biodigesters, Teflon was wrapped around the ring collar of each bottle. The capsules of the latter have been pierced with a hole to connect flexible pipes with a diameter of 10 mm, then glue is placed at the connections to avoid leaks or air ingress. A manual valve is placed at the end of each pipe to serve as a biogas sampling point.

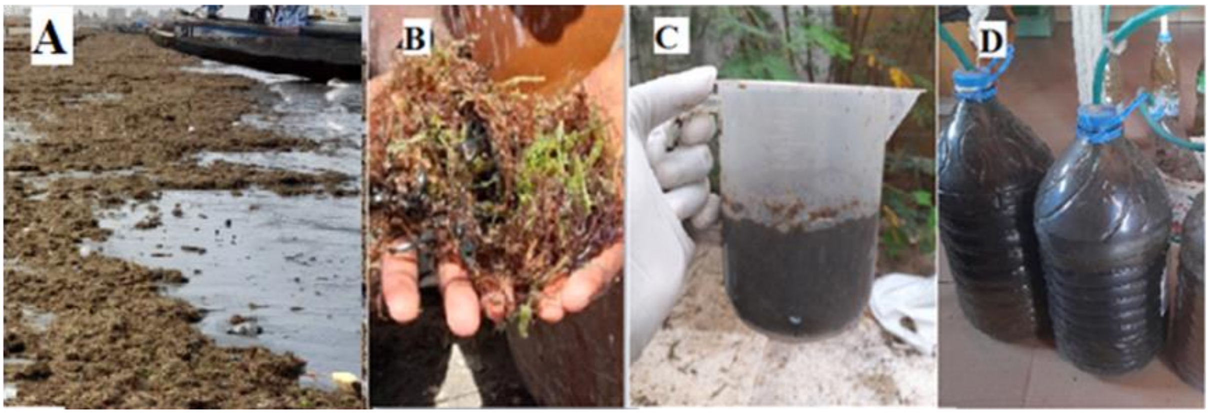

Figure 4: A: Stranded algae; B: Washed algae; C: Crushed seaweed; D: Biodigesters

For the study the substrate was mixed with water (mixing ratio 1:1). The total volume of the mixture or useful volume of the reactor is equal to 8 liters; since the reactor has a total capacity of 10 liters the two 2 liters remaining in the upper part of the digester serves as an admission chamber to store the biogas produced during the methanization process ***(see Figure 4)***. It is at the intake chamber that the sampling point *mentioned above* was connected. Gas characterization produces this at the sampling point via a gas analyzer.

The gas analyzer used is a GEM 5000-GEOTECH model dedicated in particular to measurement on anaerobic digesters.

The biogas analyzer measures the concentrations of different gas produced in the fermenter: methane (CH_4), carbon dioxide (CO_2), oxygen (O_2) and hydrogen sulfide (H_2S). Methane and carbon dioxide have measurement ranges from 0 to 100%. As for oxygen, it has a range between 0 and 25%. That of H_2S is between 0 and 5000 ppm (part per million). There are also the balls which represent the other gases. The device is also used to measure pressures between -500 mbar to 500 mbar. The analyzer is equipped with GAM software (Gas Analyzer Manager Software), so the data can be retrieved from the computer using a USB port [15].

Results and Discussions

Physico-chemical characteristics of the substrate

The results presented in ***table 1***. allow us to see the specific composition of this substrate through its dry matter and water content, its organic matter, its mineral matter, its total organic carbon and its total organic nitrogen. It is these last two parameters which will make it possible to determine the carbon-nitrogen ratio.

Dry matter and moisture content

The consistency (more or less solid state) of the substrate depends on its dry matter content. For this reason, biogas production technologies are divided into two categories: wet fermentation and dry fermentation [6].

The algae studied had 52.20 ± 1.18% dry matter. Furthermore, for reasons of mobility and/or substrate imports, humidity is a limiting parameter in relation to certain health standards. The latter had led Terrell M. et al. to dry the sargassum in the sun for two weeks before carrying out the physicochemical characterization. They obtained a dry matter content of 79.30 ± 0.93 wt% [16].

Given the water content of stranded algae, we can say that methane fermentation is the best technique for recovering this waste compared to incineration because until now burning water is not necessarily very interesting.

Organic matter (OM) and mineral matter (MM)

During methanization, only the biodegradable fraction of organic matter will be transformed into biogas. The resistant organic matter is preserved, which allows a large part of the humus to be retained after methanization. Thus, a richness in organic compounds (i.e. 70%) is a considerable asset for methanization [16, 13].

However, in this study, the substrate studied has low organic matter contents 40% and deviates slightly from the results of previous work [16, 17]. But this value remains much higher than the value of cow manure, which is the substrate of choice for the national biogas program in Senegal. We found concentration values for cow dung that varied between 25 and 30% of volatile matter depending on its state [17, 18].

Indeed, the difference in composition or concentration observed seems to be logical. Because each biomass has biological molecules that are specific to it and whose content and structure vary depending on several factors such as the growth state of the plant or even its cultivation or proliferation conditions [19].

Added to this is the fact that algal biomass is not a fossil resource but rather a living material which then contains water and organic matter. As a result, this biomass washed up on the beach decomposes, which also influences their chemical composition and requires the implementation of adequate storage and conservation strategies for controlled and stable production of biomethane.

The C/N ratio

Our marine biomass has a C/N ratio that is below the ideal C/N range (20 to 30) to maintain optimal microbial fermentation conditions. In other words, the substrate presents a significant quantity of nitrogen, which can cause the formation of compounds that inhibit methanization (ammonia and ammonium) [6, 13, 20]

Table 1: Physicochemical characteristics of stranded algae

Characteristic	Algae
Dry matter (%)	52.20 ± 1.18
Wet Matter (%)	47.18 ± 1.18
Organic Matter (%/DM)	40.34 ± 1.83
Mineral Matter (%/DM)	59.53 ± 1.83
Total Organic Carbon (%/DM)	53.71 ± 1.28
Total Organic Nitrogen (%/DM)	3.60 ± 0.14
C/N	14.92 ± 0.78

Evolution of the production and composition of biogas

When the raw material was introduced into the reactor, the pH was equal to 7.21. During anaerobic digestion the temperature of the digesters is mainly determined by the climate, more precisely the ambient temperature of the medium. The temperature variation in the shade turns around the average of 28°C.

Composition of biogas

The graph below ***(see Figure 5)*** shows that biogas is a mixture of methane, carbon dioxide hydrogen sulfide H2S, water vapor and ammonia NH3 [21]. The proportions of this mixture vary constantly depending on environmental conditions.

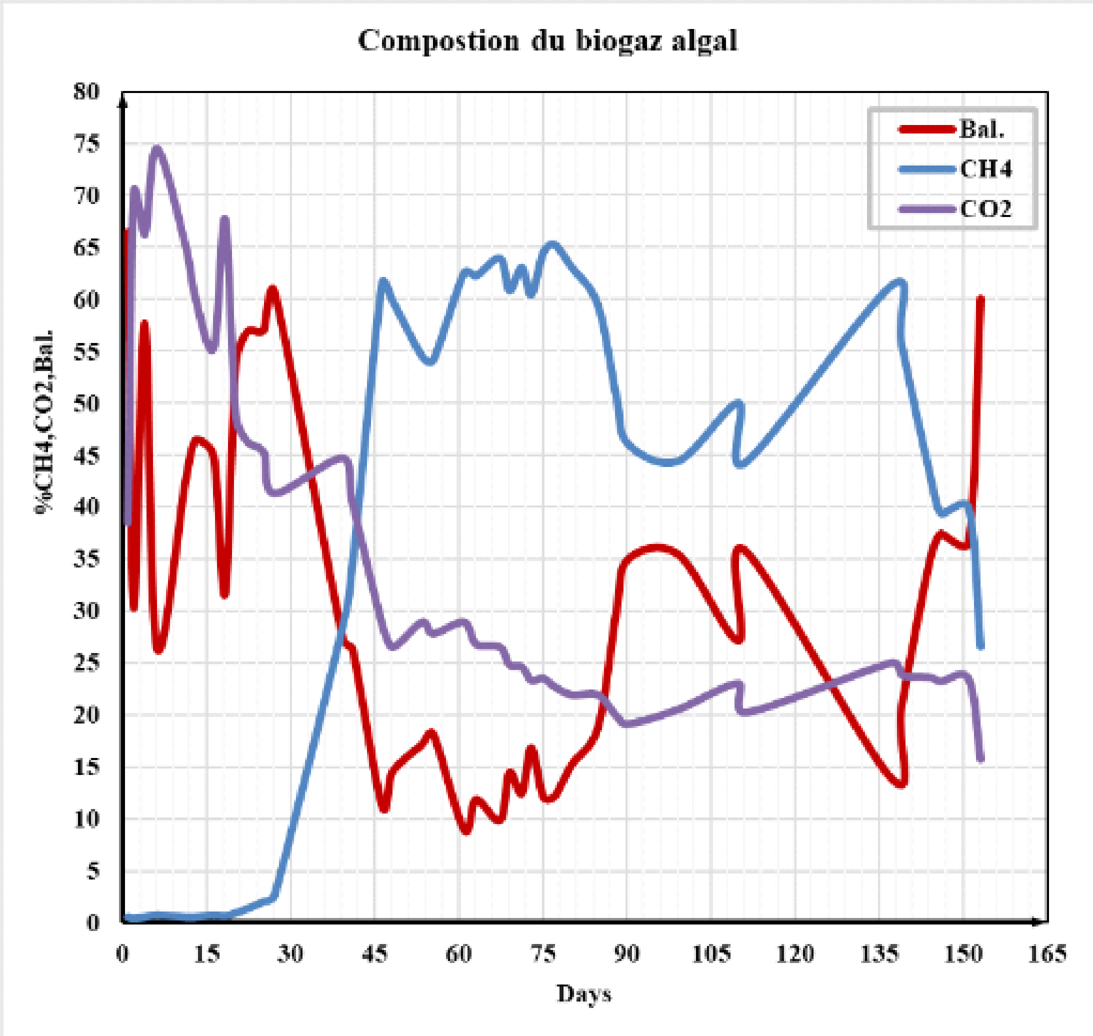

Figure 5: Composition of biogas

We can see in ***Figure 5*** the daily evolution of the biomethane concentration during biogas production. This evolution can be divided into three phases:

Latency phase:

It lasted almost 1 month. Very low methane production (less than 5%) was recorded during this phase. This period corresponded to the liquefaction phase of the substrate during which hydrolysis and acidogenesis take place. A priori upon loading and closing of the digester, decomposition is aerobic, in the presence of oxygen, followed by anaerobic decomposition in the absence of oxygen, for the remainder of its stay in the reactor. Polymeric organic matter is first broken down by microorganisms into oligomers and monomers which are then degraded with a majority production of CO_2, H_2O and energy. [22, 23, 24]

Exponential phase:

For 15 days after just the latency phase, we see a very rapid daily change in the percentage of methane contained in the biogas produced. This evolution would be reflected by an intense growth and activity of methanogenic bacteria, if we compare these results with the results of the work of BELKADI, Mohammed EL Amin who studied in his thesis the evolution of the number of bacteria in the fermentation process micro algae [25].

Stagnation phase:

the production conditions seem to be reached because it allows 65% of methane to be accounted for in biogas production which stabilizes around 60% over a fairly long period of 45 days and then slowly decreases under the effect of the exhaustion of the digestion substrate constituting the source nutrient and energy of the The proportions of methane recorded in this biogas with the stranded macro-algae are similar to those obtained by several authors, although we were not in optimized conditions [8, 16, 17, 20].microbiological flora responsible for the production of biomethane.

It would be important to note that throughout the process of methanization of this marine biomass, excessive concentrations of hydrogen sulphide (H_2S), which are greater than 5000 ppm the measurement limit value of the device, were rerecorded. It is reported in the list of Clinical signs of toxicity of hydrogen sulfide H_2S in humans: that short-term exposure to 1000 ppm causes death within a few minutes [8]. So, the desulfurization of this biogas is imperative before its use as fuel.

The production of biogas in the coastal areas of Senegal can constitute an alternative source of fuel for the processing of fishery products such as smoked and salted fish. For such use, the biogas produced must be flammable, that is to say rich in methane.

The biogas can begin to bubble when the CH_4/CO_2 ratio reaches a value of 0.6 but the fire could only be kept burning if the relative pressure of the biogas is greater than 20 mbar. Hence the interest in studying both the quantity and quality of the biogas produced.

Methanogenic potential

The methane potential of macro-algae was estimated to 0.787NLCH4/ kgVS (standard liter of methane per kilogram of organic matter) at a temperature of 28°C. It was determined from the gas pressure and the percentage of methane obtained with the biogas analyzer.

Figure 6 shows both the daily evolution of the ratio of the two majority gases in the biogas and the plot of the cumulative relative pressures which reflects the sum of the daily measurement of the quantity of biogas collected in the gasometer or volume admission chamber constant (2 liters).

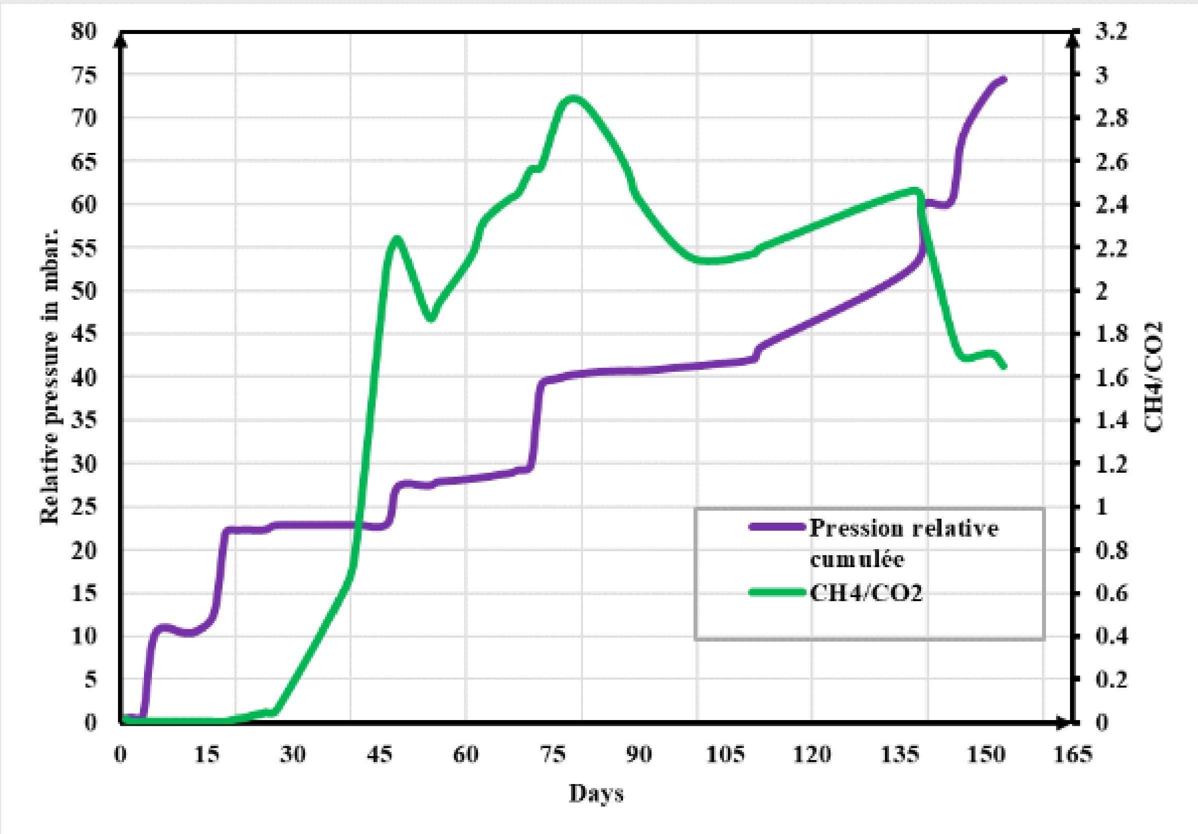

Figure 6: Kinetics of biogas production

The shape of the cumulative pressure curve presents changes in stages. This reflects the kinetics of conversion of organic matter into gas.

Indeed, biomass is composed of a carbon skeleton on which other elements are attached in variable proportions: essentially hydrogen and oxygen (carbohydrates and fats), nitrogen (proteins), phosphorus (nucleic acids) or sulfur (certain amino acids). These elements of organic matter do not have the same gas energy potential [26, 27] :

- Fats have the highest biogas production efficiency and are rapidly degraded;
- Carbohydrates and proteins have faster conversion rates but produce less biogas;
- Substrates containing lignin and cellulose will take much longer to be degraded, they require a high residence time.

Thus, the variation in biogas production would depend on the biodegradability of the different compositions of algal organic matter.

Therefore we can read from the two figures ***(Figure 5& Figure 6)*** that if the desired goal is to obtain a complete decomposition of the organic constituents or a maximum yield in gas production, we need a longer residence time. So, the objective must therefore be to obtain optimal degradation with a biogas rich in methane. The interval of the two intersections of the cumulative relative pressure curve and that of CH4/CO2 seems to indicate the necessary time for which the substrate must remain in the digester.

In other words, to maintain the continuous system with flammable gas production, it is essential to take into account when designing the recovery unit that this marine biomass has a latency time of 30 days plus a recovery time. 90 day stay. Hence, this work can explain the yield improvements noted by Alberto Vergara-Fernàndez et al. by carrying out the physical separation of the phases of algae methanization into two phases: ***Figure 7***.

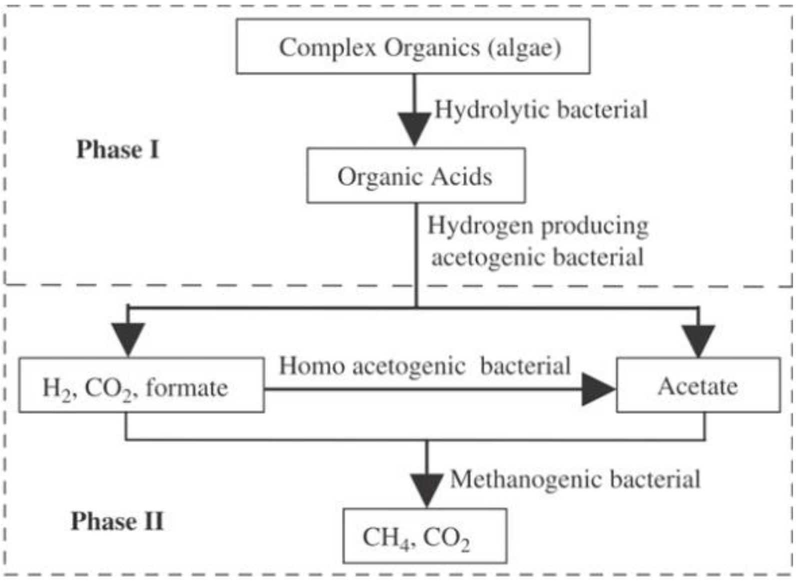

Figure 7: methanization process [28]

However, the quantity of biogas collected through this study is low compared to the experimental values reported by Robin Sallio. The experimental methanogenic potentials of macroalgae were generally between 150 and 200 LCH4/ kgVS [8]. This situation of low CH4 levels observed during the present study could be explained by the fact that several of these values are obtained under optimized conditions and generally at mesophilic temperature to have the best possible yields. It would be interesting to do the same in order to better reconcile the results.

Conclusion

The West Africa Sargassum Technical Working Group dreams that one day seaweed will not only be seen as an emerging environmental challenge, but as a "new normal" opportunity for green wealth creation.

In this context, this work shows that it is indeed possible with an appropriate management strategy. Anaerobic digestion represents a basic technology allowing the exploitation of invasive macroalgae in the commune of Joal-Fadiouth. As well as many other parts of the Atlantic coast of Africa.

Despite, a C/N ratio of 14.92 ± 0.78 and under ambient temperature and pressure conditions; the treatment of this marine waste by anaerobic digestion led to the production of biogas rich in methane (more than 60%) or a methanogenic potential of 0.787 LCH4/kgVS at a temperature of 28°C. the substrate studied also had 52.20 ± 1.18% dry matter and an average organic matter concentration value of 40% relative to its dry content. The qualitative and quantitative analysis of biogas production showed that to ensure continuous operation with flammable gas production, it is essential to take into account when designing the valorization unit through the

methanization of stranded algae, that this marine biomass has a latency time of 30 days plus a residence time of 90 days under conditions which respect the sixth principle of green chemistry.
Desulfurization of biogas derived from stranded algae is necessary for safe and sustainable use. It is also important to know that this biomass washed up on the beach decomposes, which influences their chemical composition and requires implementing adequate storage and conservation strategies for controlled and stable production of biomethane.
This research work opens several avenues for research into optimizing the production of algal biogas because it is not in the optimal conditions for methanization.

Acknowledgment
Thanks to the National Integrated Waste Management Company (SONAGED) for its support.

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