International Scientific Journal
Journal of Environmental Science
http://environment.scientific-journal.com/

Energy recovery from algal waste

Jose Luis Salgueiro, Antonio Larramendi, , Ángeles Cancela, Ángel Sánchez
Chemical Engineering Department
EEI, University of Vigo
Vigo, Spain

Leticia Pérez
Sustainable Energy Technological Center
EnergyLab
Vigo, Spain

Abstract*— Marine macroalgae are an abundant resource in coastal areas. In most cases, this algal matter is removed from the beaches and treated as waste. The collected algae constitute a source of biomass with a high potential to produce energy. Three possible options for energy recovery from residual algal matter have been analyzed: to obtain biodiesel, bioethanol and pellet manufacturing. The energy recovery from macroalgae confers a saving on current disposal costs as a residue and an environmental benefit because it is Kyoto Protocol compilant. Six different marine algae have been used as raw materials: *Fucus Spiralis, Pelvetia Canaliculata, Saccorhiza Polyschides, Enteromorpha (Ulva), Polysiphonia Lanosa* and *Calliblepharis Ciliata.

Macroalgae have a high content of carbohydrates and low lignin content, which make them to be a suitable substrate in the fermentation process for bioethanol production. To obtain this biofuel, chemical processes –such acid hydrolysis– and biological processes –enzymatic hydrolysis and alcoholic fermentation– have been tested. Concentrations of sulfuric acid of 0.05, 0.2 and 0.5M have been used in the acid hydrolysis processes. The results obtained show that higher production of bioethanol was achieved with the highest concentration of acid autoclave conducted hydrolysis. A greater amount of ethanol was managed by *Fucus Spiralis* algae when an acid hydrolysis process was followed by a fermentation in an orbital incubator. In the case of fermentation with intermediate enzymatic hydrolysis, the *Calliblepharis Ciliata* algae produces the highest bioethanol amount. On the other hand, very low conversion percentages of oil to biodiesel were determined for all studied algal species.

Finally, with the objective of making pellets and evaluating its burning quality, intrinsic characteristics of each species (calorific value, ash content, volatile content and fixed carbon content) were tested. *Fucus Spiralis, Pelvetia Canaliculata* and *Calliblepharis Ciliata* were found as the most suitable species for making pellet. The quality of pellet obtained was similar to that obtained by other raw materials.

Keywords—bioethanol; biodiesel; pellets; macroalgae;

I. INTRODUCTION

Energy supply is a constant concern because there is a strong dependence on fossil fuels for living and manufacturing [1]. Dependence on this fuel presents many environmental problems and resources to obtain them are limited [2]. Therefore, depletion of fossil fuel, the increase of energy consumption and global warming, requires the search for different types of efficient alternative energies. For that, it is necessary new sources of energy environment friendly, effective, and cost afordable [3].

Macroalgae biomass is a promising candidate to feedstock, offering a variety of solutions for bioenergy, such as biodiesel, bioethanol and pellets, in other words, a source of renewable energy [4]. It is known that, certain species of macroalgae have carbohydrates high and lignin low contents, suitable for the biofuels conversion processes [5]. These organisms can show high growth rate and can be found on coastal areas, where they are handled as a residues. The highest production of seaweed forests is on the Pacific coast [6], although in Asia large quantities of macroalgae are being cultivated on large scale. For this reason, it is important that the raw materials considered are not expensive, so the production is viable.

In addition, dying macroalgae offer many advantages over terrestrial crops: its cultivation requires no farmland, fresh water or fertilizers. In this way, there have no possible comparison on the biomass production and the availability of resources.

This research focuses on the exploitation of marine macroalgae as feedstock in three possible forms of biofuels: biodiesel, bioethanol and pellets. To do this, six different macroalgae have been studied: *Fucus Spiralis, Pelvetia Canaliculata, Saccorhiza Polyschides, Enteromorpha (Ulva), Polysiphonia Lanosa* and *Calliblepharis Ciliata.*

II. MATERIALS AND METHODS

A. Raw materials

Marine macroalgae were obtained from the coastal areas and and banks of Galicia, Spain. Collected algae samples were: *Fucus Spiralis, Pelvetia Canaliculata, Saccorhiza Polyschides, Enteromorpha (Ulva), Polysiphonia Lanosa* and *Calliblepharis Ciliata.* Biomass was washed and dried before being sliced into small pieces. After that, samples were stored in airtight containers before use.

B. Obtaining Bioethanol

Following, the different processing steps for the obtaining of bioethanol are shown.

1) Acid hydrolysis

In order to improve the production of bioethanol, two different pre-treatment methods were analyzed: autoclave and thermostatic bath.

In the autoclave pretreatment, 15 g of dried algae was mixed with 150 mL of 0.05, 0.2 or 0.5 M H_2SO_4 and autoclaved (Selecta model Micro 8) at 121 ºC and 1.5 bar for 15 min. Then, the mixture was cooled into an ice bath to room temperature. On the other hand, for the experiments conducted in thermostatic bath, algae biomass was also mixed (the same concentrations) and then acid hydrolyzed in a thermostatic bath (Ovan Model B105E) at 30 ºC, for 20 min.

2) Neutralization

Hydrolysate was neutralized by reaction with 2M NaOH. This process was performed at room temperature using a magnetic stirrer (Hanna model HI 190M) to facilitate the NaOH solution.

3) Centrifugation I

After that, solid products were separated from the liquid by centrifugation for 10 min at 4000 rpm. This process was performed in centrifuge tubes (50 mL) by an angular centrifuge (JP Selecta model Cencom II).

4) Enzymatic hydrolysis

The enzyme used was Cellulast®, at 2% (dry weight) of the sample. Enzymatic hydrolysis experiments were conducted with the solid product resulting from centrifugation, enzyme, and 50 mL of H_2O per 10 g of solid sample obtained. The temperature and pH were adjusted to 55 ºC and 4.5-5 respectively. Hydrolysis was carried out in a thermostatic bath for 72 h.

5) Centrifugation II

After 72 hours, the samples were left to room temperature and centrifuged for 10 min at 4000 rpm in angular centrifuge. The liquid fraction was reserved and the solid one was discharged.

6) Fermentation

The centrifuged liquid samples were fermented using *Saccharomyces Cerevisiae* strain to obtain ethanol. This process was carried out in two ways: vacuum fermentation and incubation shaker.

a) Vacuum fermentation

The vacuum fermentation was initiated by adding 36 mL of neutralized liquid, 0.4 g of *Saccharomyces Cerevisiae* strain and 2 mL of 0.05 M $NaCH_3COO$ buffer solution. This process was performed in vacuum flasks with magnetic stirring with a (OVAN Maxi Model OL30-ME) heater for 72 h at 40 °C. In such a way, the alcoholic fermentation happens under anaerobic conditions.

b) Incubation shaker

In this case, the fermentation was conducted in flasks equipped with a valve that allows CO_2 to be released during the fermentation, guarantying anaerobic conditions.

A liquid sample of 18 mL was mixed with 0.2 g *Saccharomyces Cerevisiae* strain and 1 mL of 0.05 M $NaCH_3COO$ buffer solution. The fermentation temperature was kept constant at 40 ºC for 72 h in an (OVAN Model I10-OE) incubation shaker under agitation, at 90 rpm.

7) Distillation

Once the fermentation process was completed, the product obtained was distilled in a distillation set. The ethanol concentration was determined by refractometry.

The different experiments conducted in order to obtain bioethanol are listed in Table I.

TABLE I. PROPOSED EXPERIMENTS TO OBTAIN BIOETHANOL

Exp.	Design of experiments				
	Acid hydrolysis		*Enzymatic hydrolysis*	*Fermentation*	
	Autoclave	*Thermostatic bath*		*Vacuum ferment.*	*Incubation shaker*
1	-	*yes*	-	-	*yes*
2	*yes*	-	-	-	*yes*
3	-	*yes*	-	*yes*	-
4	*yes*	-	-	*yes*	-
5	-	*yes*	*yes*	-	*yes*
6	*yes*	-	*yes*	-	*yes*
7	-	*yes*	*yes*	*yes*	-
8	*yes*	-	*yes*	*yes*	-

C. Obtaining Biodiesel

The biodiesel production was carried out in two-steps: first, lipid extraction was performed by extraction equipment and then the lipids obtained were transesterified.

1) Lipid extraction

The method chosen for extract the lipids from macroalgae biomass was Soxhlet extraction. The effect of two organic solvents were studied: n-C_6H_{12} and CH_3OH. An amount of 10 g was extracted with 200 mL of solvent. Extractions were conducted for 4 h at 65 °C. After that, the obtained product was distilled in order to remove the solvent and recover the lipid.

2) Transesterification

The oil obtained was subjected to transesterification using NaOH as catalyst. The transesterification reaction started with a mixture of algae oil: CH_3OH 6:1 (molar ratio) and 1 wt% NaOH. This reaction was heated at 60 ºC for 5 h at constant stirring. When the reaction was completed, the mixture was filtered to remove the solid particles. Finally, glycerin (bottom layer) was separated and biodiesel mixture (top layer) was washed with warm water with the aim to remove CH_3ONa residue.

D. Obtaining Pellet

In order to get the maximum usage, algal residues from biodiesel production were used as raw material for pellets manufacturing. Algal biomass was subjected to different tests according to the following standards: volatile matter [7], ash

content [8], heating power [9]. The fixed carbon was determined by the equation (1):

$$\text{Fixed carbon \%} = 100 - \text{Volatile matter \%} - \text{Ash \%} \quad (1)$$

III. RESULTS AND DISCUSSION

A. *Bioethanol*

Several experiments, described in Table I, were conducted to obtaining bioethanol. Fig. 1 shows the data obtained in experiment 1. It can be observed that with all species of macroalgae used in acid hydrolysis by thermostatic bath followed by direct fermentation and incubation in a shaker, the refraction index increased with acid concentration. The highest concentration of ethanol was reached by *Saccorhiza Polyschides* (1.3401) when a 0.5M acid concentration was used.

In the same way, when this type of fermentation process was combined with an acid hydrolysis process in an autoclave, a greater amount of bioethanol was obtained. When 150 mL of 0.5 M H_2SO_4 was used. As can be seen from Fig. 2, *Fucus Spiralis* algae obtained the highest refraction index, 1.3456, that is, the highest concentration of alcohol. This means that autoclave treatment improves the performance of anaerobic fermentation, because it extracts a greater quantity of carbohydrates. Even so, the ethanol quantities obtained are very low.

On the other hand, acid hydrolysis was carried out followed by a vacuum fermentation experiments 3 and 4. Fig. 3 and 4 show the refractive index achieved in function of the pH.

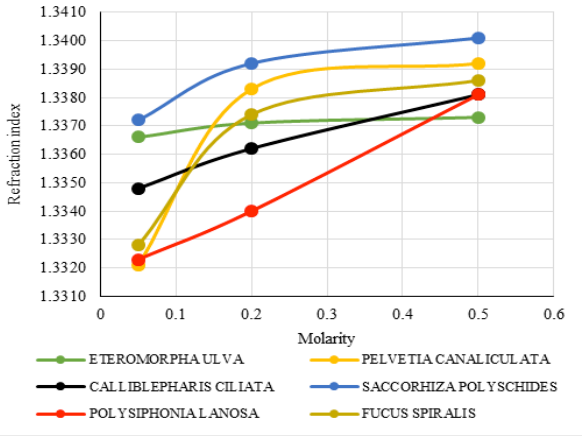

Fig. 1. Bioethanol efficiency of acid hydrolysis by thermosthatic bath and fermentation in incubator shaker.

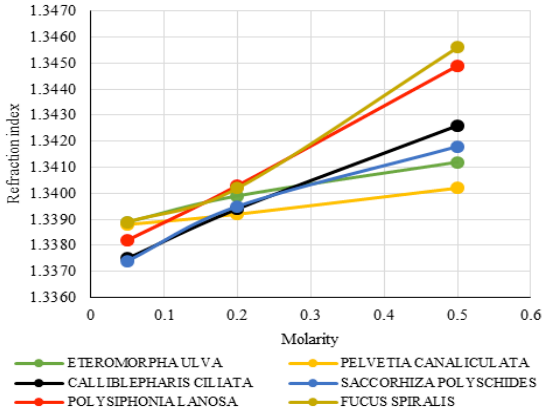

Fig. 2. Bioethanol efficiency of acid hydrolysis in autoclave and fermentation in incubator shaker.

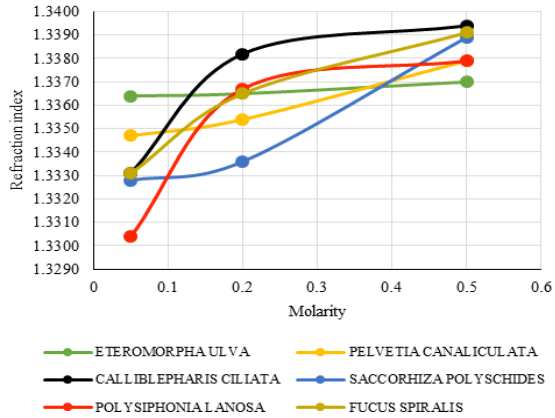

Fig. 3. Bioethanol efficiency of acid hydrolysis in thermosthatic bath and vacuum fermentation.

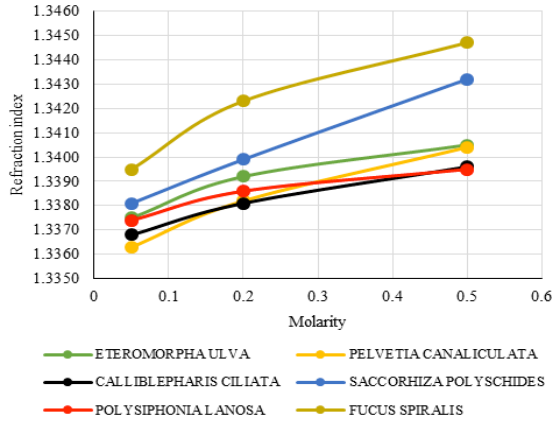

Fig. 4. Bioethanol efficiency of acid hydrolysis in autoclave and vacuum fermentation.

It can be observed that both processes show similar behaviour to the previous cases but performance is lower.

Based on the observed data, *Fucus Spiralis* macroalgae is the most suitable algae for bioethanol production by a hydrolysis plus fermentation process. In addition, the method used for fermentation had little influence on the results, being higher the alcohol content reached in the fermentation carried out in the incubator shaker.

Consequently, with the objective of improving the ethanol production, enzymatic hydrolysis has been added. The same test combination has been performed but adding this treatment. Fig. 5, Fig. 6, Fig. 7 and Fig. 8 show the results obtained. As expected, this treatment improves the performance to obtain bioethanol. In this case, *Calliblepharis Ciliata* algae reached the highest bioethanol content with a refraction index of 1.3461 by acid hydrolysis in autoclave followed by an enzymatic hydrolysis and finally, a vacuum fermentation was conducted. However, the amounts of ethanol obtained remain low.

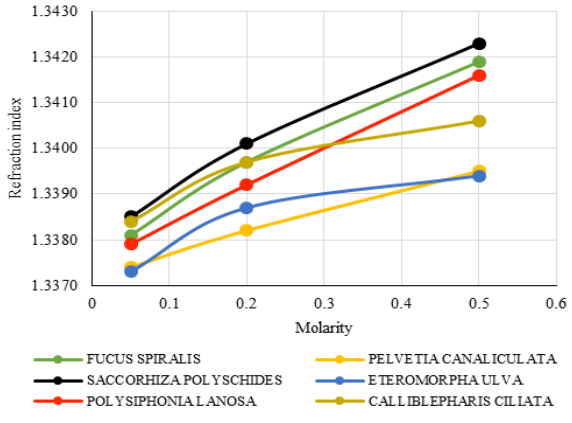

Fig. 5. Bioethanol efficiency of acid hydrolysis in thermosthatic bath, enzymatic hydrolysis and fermentation in incubator shaker.

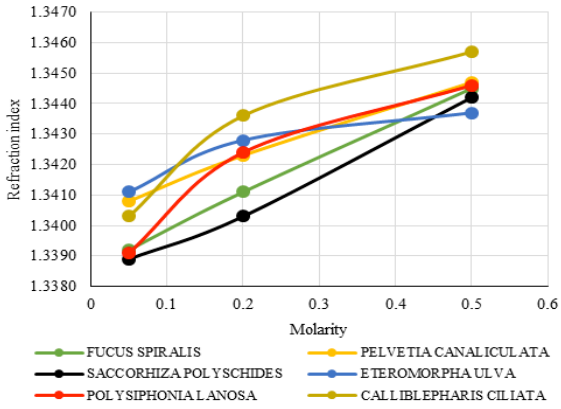

Fig. 6. Bioethanol efficiency of acid hydrolysis in autoclave, enzymatic hydrolysis and fermentation in incubator shaker.

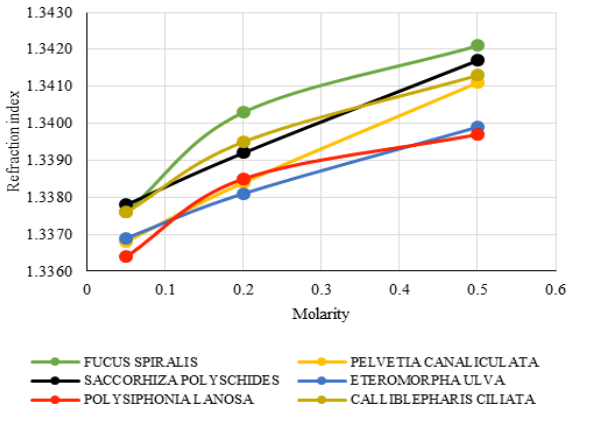

Fig. 7. Bioethanol efficiency of acid hydrolysis in thermosthatic bath, enzymatic hydrolysis and vacuum fermentation.

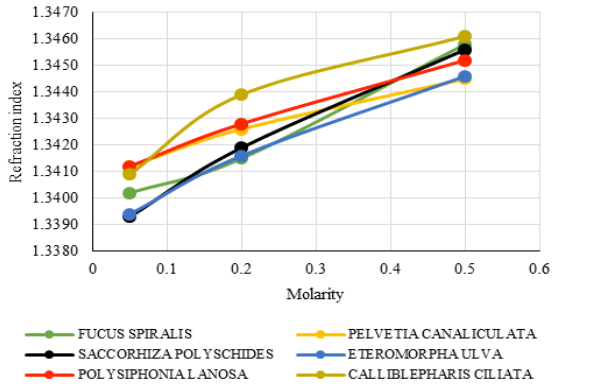

Fig. 8. Bioethanol efficiency of acid hydrolysis in autoclave, enzymatic hydrolysis and vacuum fermentation

B. Biodiesel

In this research, biodiesel was obtained by extracting lipids from the 6 macroalgae species and subsequent transesterification. Lipid amount of seaweeds extracts made with organic solvents as CH_3OH or n-C_6H_{12} are shown in Table II. In all cases, the polar solvent used (CH_3OH) has managed a much higher lipid extraction than non-polar solvent, n-C_6H_{12}. Probably, a greater amount of lipids could be extracted from these macroalgae species using a mixture of a polar and a non-polar solvent based on data published by other authors [10].

TABLE II. PERCENTAGE OF LIPID EXTRACTED BY SOXHLET EQUIPMENT

Macroalgae	**% Lipid extracted**	
	CH_3OH	***n-C_6H_{12}***
Fucus Spiralis	7.53	1.96
Pelvetia Canaliculata	10.86	1.24
Saccorhiza Polyschides	9.60	0.42
Eteromorpha Ulva	8.47	0.29
Polysiphonia Lanosa	8.75	0.75
Calliblepharis Ciliata	5.97	0.27

As can be seen in the table, the highest lipid extraction was achieved with *Pelvetia Canaliculata* algae (10.86%), followed by *Saccorhiza Polyschides* algae (9.6%). Another improvement to increase lipid extraction would be to subject the biomass to a pretreatment before to extraction. This pretreatment could be high-pressure homogenization, ultrasonication, microwaving, and acid treatment [11]. After soxhlet extraction, the lipids were subjected to the transesterification process. The results obtained after this process indicate a very low yield, showing conversion rates of 1.65 to 5.14%.

C. Pellet

In this section, the intrinsic characteristics of the macroalgae used were analyzed to assess their use as feedstock for pellets manufacturing. Physical and chemical parameters of the different macroalgae are shown in Table III.

TABLE III. CHARACTERISTICS OF PELLETS FROM EXTRACTION

Macroalgae	*Volatile matter (%)*	*Ash content (%)*	*Fixed carbon (%)*	*HHV[a] (kJ/kg)*	*LHV[b] (kJ/kg)*
Fucus Spiralis	70.06	19.28	10.65	13235.30	11912.84
Pelvetia Canaliculata	71.42	19.39	9.18	12225.06	10902.6
Saccorhiza Polyschides	48.72	47.36	3.90	8623.236	7300.87
Eteromorpha Ulva	54.73	42.69	2.56	8173.26	6850.80
Polysiphonia Lanosa	52.07	45.87	2.04	9543.03	8220.57
Calliblepharis Ciliata	69.32	25.49	5.18	13175.63	11853.18

[a] HHV: High heating value

[b] LHV: Low heating value

Resulting values were compared to the Standard [12] to evaluate their possible use as fuel for biomass boilers. Based on the data obtained, none of the algal pellets would be suitable as fuel in biomass boilers. This means that the algal pellets could be adapted to the requirements established by the standard if they are mixed with other sources [13]. In this case, the most suitable candidates to make pellets could be *Fucus Spiralis, Pelvetia Canaliculata* and *Calliblepharis Ciliata.*

IV. CONCLUSIONS

This study investigated different methods of energy recovery from marine macroalgal species. The results obtained showed that acid hydrolysis followed by enzymatic hydrolysis and a fermentation process improve the bioethanol production. In regard to lipid extraction, the use of a polar solvent like CH_3OH achieved better results than one apolar like n-C_6H_{12}. The process of obtaining biodiesel in two stages managed very low yields in the six species of macroalgae studied. Respect to the manufacture of pellets, the marine algae studied are not adequate by themselves as fuel for boilers, however they could be used in combination with other sources.

REFERENCES

[1] M. Su, M. Zhang, W. Lu, X. Chang, B. Chen, G. Liu, Y. Hao, Y. Zhang, "ENA-based evaluation of energy supply security: Comparison between the Chinese crude oil and natural gas supply systems," Renew. Sustain. Energy Rev., vol. 72, 2017, pp. 888–899.

[2] R. Bibi, Z. Ahmad, M. Imran, S. Hussain, A. Ditta, S. Mahmood, A. Khalid, "Algal bioethanol production technology: A trend towards sustainable development", Renew. Sustain. Energy Rev., vol. 71, 2017, pp. 976–985.

[3] P. Fasahati, H.C. Woo, J.J. Liu, Industrial-scale bioethanol production from brown algae: Effects of pretreatment processes on plant economics, Appl. Energy., vol. 139, 2015, pp. 175–187.

[4] M. Enquist-Newman, A. Marie, E. Faust, D.D. Bravo, C.N.S. Santos, R.M. Raisner, A. Hanel, P. Sarvabhowman, C. Le, D.D. Regitsky, S.R. Cooper, L. Peereboom, A. Clark, Y. Martinez, J. Goldsmith, M.Y. Cho, P.D. Donohoue, L. Luo, B. Lamberson, P. Tamrakar, E.J. Kim, J.L. Villari, A. Gill, S.A. Tripathi, P. Karamchedu, C.J. Paredes, V. Rajgarhia, H.K. Kotlar, R.B. Bailey, D.J. Miller, N.L. Ohler, C. Swimmer, Y. Yoshikuni, "Efficient ethanol production from brown macroalgae sugars by a synthetic yeast platform", 2014.

[5] M.G. Borines, R.L. de Leon, J.L. Cuello, "Bioethanol production from the macroalgae Sargassum spp.", Bioresour. Technol., vol. 138, 2013, pp. 22–29.

[6] S. Kraan, "Mass-cultivation of carbohydrate rich macroalgae, a possible solution for sustainable biofuel production", Mitig. Adapt. Strateg. Glob. Chang, vol. 18, 2013, pp. 27–46.

[7] UNE-EN ISO 18123:2016. Solid biofuels - Determination of the content of volatile matter. AENOR.

[8] UNE-EN ISO 18122:2016. Solid biofuels - Determination of ash content. AENOR.

[9] UNE-EN 14918:2011. Solid biofuels - Determination of calorific value. AENOR.

[10] Y. Li, F. Ghasemi Naghdi, S. Garg, T.C. Adarme-Vega, K.J. Thurecht, W.A. Ghafor, S. Tannock, P.M. Schenk, "A comparative study: the impact of different lipid extraction methods on current microalgal lipid research.", Microb. Cell Fact., vol. 13, 2014, 14.

[11] M. Mubarak, A. Shaija, T.V. Suchithra, "A review on the extraction of lipid from microalgae for biodiesel production", Algal Res., vol. 7, 2015, pp. 117–123.

[12] UNE-EN ISO 17225-6:2014. Solid biofuels - Fuel specifications and classes - Part 6: Graded non-woody pellets. AENOR

[13] Á. Cancela, Á. Sánchez, X. Álvarez, A. Jiménez, L. Ortiz, E. Valero, P. Varela, "Pellets valorization of waste biomass harvested by coagulation of freshwater algae", Bioresour. Technol., vol. 204, 2016, pp. 152–156.