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Biofuel Obtained from Benthic Marine Flora *Macrocystis pyrifera* and its Characterization

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The use of energy is fundamental in the main industrial, communications and other activities, it has become an essential resource in people's lives and in the development of peoples; However, some sources of its production have negative impacts on the environment, especially fossil and mineral sources that cause a greater negative impact. In Peru, in 2019, the energy sources were natural gas (including liquids) at 64.4%, mineral coal at 0.4%, crude oil at 10%; those from natural resources: hydropower 12.7%, firewood 8.8%, bagasse 2.1%, dung with yareta 0.5% and solar energy 0.4%. The objective of the research was to obtain biofuel and characterize it from benthic marine flora, specifically from the alga Macrocystis pyrifera. The method consisted of extracting the oil from three samples of 30 g of algae with three repetitions each, followed by a transesterification process and then separating it into phases with sodium methoxide, obtaining the biofuel. The results of the characterization of the product indicated a density of 0.8999 g/mL, kinematic viscosity 2.3314 cSt at 40 ° C, acid number of 0.344 mg KOH/g, carbon residue of 0.024% m/m, sulphated ash of 0.017%. m/m calorific value from 39.40 to 39.43 MJ/kg. These characteristics meet the specifications of EN 14214, ASTM D6751, ANP N ° 7/08 and NTP 321.125.2019 (an exception for kinematic viscosity that only met the first two named). In this way, it was shown that this natural resource turns out to be a viable alternative to be used as a source of bioenergy and with a low negative impact on the environment.

1. Introduction

Seaweeds are used for multiple purposes, especially as food since ancient times in Asian peoples, and in more recent times as fertilizers, biofuels, in cosmetics and others due to their content of proteins, vitamins, lipids, polysaccharides, minerals, phenols, chlorophylls, etc. (Cuesta et al., 2016). Algae are considered as third generation biofuel sources and have the advantage that their cultivation does not require agricultural land, they avoid pollution contrary to conventional fossil fuels; the component of interest for biofuel is the lipid content they contain, so recent research is aimed at identifying the type of algae with the highest content as well as the most efficient methods for extraction. (Enamala et al., 2018). In a European project, *Dunaliella salina* was evaluated for extraction of 9-cis carotenoids, another important algal product. (Harvey and Ben-Amotz, 2020). Obtaining energy from algae biomass is a future possibility within the sustainable bioeconomy, and there are already advances in "synthetic biology" technology or fourth generation energy, which consists of genetically producing algae for biofuels.(Aro, 2016).
The mechanism of algae growth is photosynthesis, they use the energy of sunlight, have a great capacity to assimilate atmospheric CO_2 and convert it to carbohydrates, lipids and bioactive metabolites.(Ramos et al., 2021). Microalgae tend to replace fossil fuels, even with limitations, they have the advantage of being renewable and of low environmental impact (Khan et al., 2018). The types of biofuels obtained depend on the type of algae and the methodology, biodiesel is obtained from lipids (*Chorella vulgaris, anochloropsis sp* and others) followed by a process of transesterification and purification, ethanol is obtained from the hydrolysis of sugars, fermentation and purification, also biogas from anaerobic digestion; but the remaining challenge is to obtain bioethanol from microalgae biomass. (Escobedo et al., 2021). In these processes, many parameters must be

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controlled to improve efficiency, including algae cultivation. (Peñaranda et al., 2013), or solvents for the extraction (Molino A. et al., 2018).
There are studies to obtain biofuel from microalgae, in this case the objective of the study was to obtain biofuel from benthic waste, specifically from the macroalgae *Macrocystis pyrifera* (known as sargassum), and then it was characterized. The macroalgae was collected on the beaches of Marcona, where fishermen collect this species, which exists in large quantities and is expelled by the sea after it has completed its life cycle, detached from the seabed and deposited on the shores, as shown in Figure 2. It is known that on the shores of Yanyarina (Arequipa) and Marcona (Ica) beaches, 400 MT/month were deposited by the dynamics of sea waves in April 2008. (ICON-INSTITUT, 2009), later in 2017 the Artisanal Fishing Landing Administration (DPA) of Punta San Juan de Marcona, through an audiovisual of the Artisanal Fishing Community of Marcona (COPMAR), indicated that the collection of dry benthic products was one thousand MT/month. It is indicated that the Ica-Marcona region is an area of evaluation and abundance of macroalgae. (IMARPE and APROSUR, 2012). Therefore, there is a need for research to determine the viability of macroalgae in obtaining energy, identifying the optimal treatment for the transformation of biomass into energy. (Chojnacka et al., 2018).

2. Methodology

The research was carried out according to the scheme shown in Figure 1.

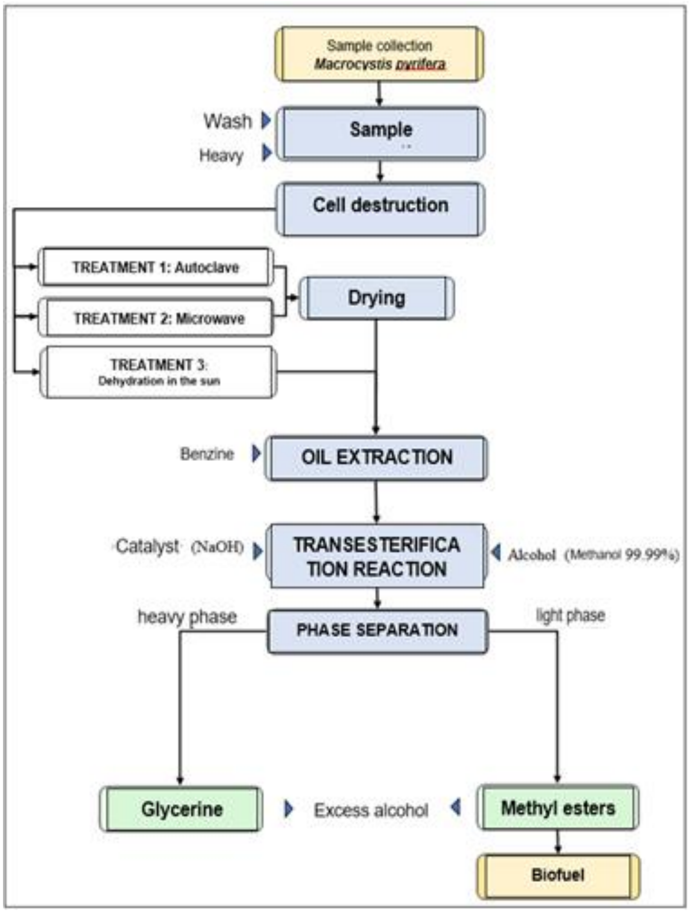

Figure 1: Schematic of the research process

Source: (PNUD Perú, 2017)

Figure 2: Macroalgae harvesting at Marcona

Figure 3: Collection of benthic residues (Macrocystis pyrifera)

2.1 Collection of the algae sample Macrocystis pyrifera

The algae were collected with the support of fishermen from the "El Arca de Noe" Sea Farmers Association at the "7 Huecos" beach in Marcona, at UTM coordinates: 15°24'29.32" S-75°0712.46" W, where benthic upwelling occurs near the shore and is washed ashore by the waves and tide. See Figure 3.

Characteristics of Macrocystis pyrifera algae:

This algae species is a benthic organism considered the largest in the world, it can grow up to 30 meters (Peña and Salgado, 2016), its growth in 21 days is up to 50cm (Barsanti and Gualtieri, 2014). The alga *Marocystis pyrifera* has taxonomic classification in the division of Phaeophyta, classified by *Phaeophyceae* (*Phaeophyceae*), order Laminariales, family *Lessoniaceae* and genus *Macrocystis* (Salavarría, 2014). This macroalgae has a greenish brown or brownish yellow color, due to the large amount of xanthophylls, including fucoxanthin and flavoxanthin (Ortiz, 2011) which is why it is commonly called brown algae. Its growth begins in the rocky substrate in which it is strongly fixed (Salavarría, 2014) and at a depth of approximately 25 meters from the intertidal; it serves as a substrate for the habitats of mollusks, fish, and other marine fauna, it is found throughout the North Pacific, from Alaska to Mexico, the coast of South America from Peru to Argentina, and in isolated regions such as South Africa, Australia and New Zealand and in sub-Antarctic islands (Peña and Marín, 2016)

2.2 Cellular destruction

At this stage, cell disruption was carried out by three methods as shown in Figure 4: autoclaving, microwave and solar dehydration.

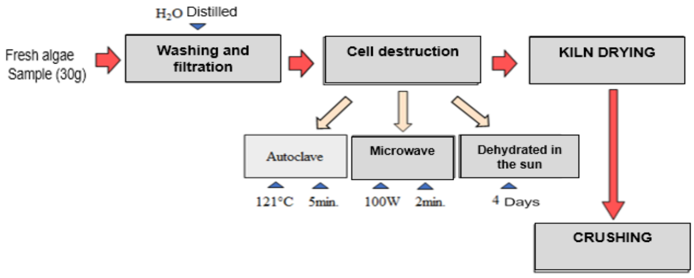

Figure 4: Cellular destruction

2.3 Extracción de aceites con solvente por Soxhlet

The crushed samples were subjected to fatty acid extraction, using the solvent benzine in a soxhlet apparatus, at 190°C in a time of 14 hours with 10 solvent cycles for each sample. Then the extract was taken to the solvent evaporation process at a temperature of 37°C in 3 hours. The final extract was cooled and weighed corresponding to the oil obtained from the algae. To calculate the percentage of acids and fats extracted, Eq (1) was used.

$$\%\ Acid\ and\ Fats = \frac{\text{mass of the oil obtained}}{\text{mass of the wet sample}} * 100 \tag{1}$$

It was determined that algae subjected to sun dehydration allowed obtaining more oil from the algae.

2.4 Transesterification of algal oil

For this process, 0.8463 g of sodium hydroxide was used as catalyst and 50 mL of 99.99% methanol for the transesterification of the algae oil, then the separation is performed to finally obtain the biofuel product. See Figure 5.

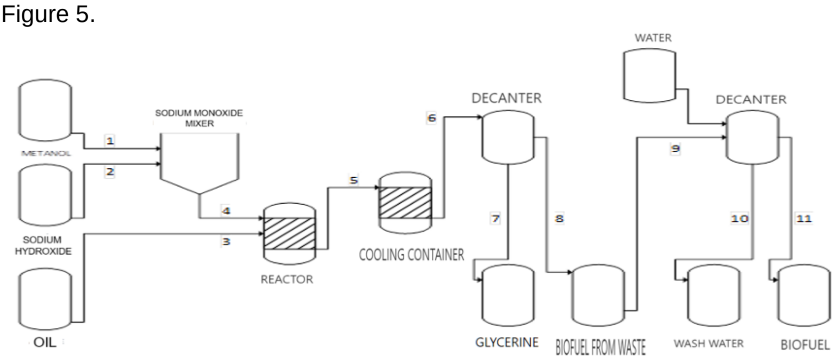

Figure 5: Transesterification process of Macrocystis pyrifera algae oil.

2.5 Biofuel properties calculation

The following were determined for the biofuel obtained: acidity, carbon residue, ash, density, kinematic viscosity and calorific value.

3. Results

3.1 Operating conditions in the process

The operating conditions for the production of biofuel from benthic marine flora, specifically from *Macrocystis pyrifera* algae, in the cell destruction stage, according to the methods presented in Table 1.

3.2 Soxhlet Extracted Oil Content

Table 2 shows the oil content obtained taking into account the solar destruction treatment. It is determined that the best result is obtained in the case of solar dehydration.

Table 1: Operating conditions in the cell destruction stage.

Indicators	Autoclave	Microwave	Sun Dehydration
Temperature	121°C	-	21°C
Power	-	100W	-
Time	5 min.	2 min.	4 days

Table 2: Soxhlet extracted oil result

Treatment of cell destruction	Wet mass of algae (g)	Oil content (benzine solvent)	
		Weight (g)	Acids and fats (%)
Autoclave	30	0.0144	0.0482
Microwave	30	0.0119	0.0397
Sun Dehydration	30	0.0168	0.0561

From the amount of oil obtained from the algae, 250 mL were taken to carry out the transesterification process, at the end the conversion to 100 % biofuel was obtained, this happens when the process is carried out with catalyst to stop the washing of the biofuel and the complete elimination of water, a value very close to that obtained in another research that used the same process (catalyst and alcohol) obtained biofuel from used cooking oil. (López et al., 2015).

3.3 Biofuel density

Using the pycnometer, the density of the biofuel was determined at 25 °C and 40 °C, being lower at 40 °C (see Table 3). This value will be used to determine the kinematic viscosity.
Density is critical to the use of biofuels when used in engines as it affects power, emissions and consumption. (Poma, 2004), depends on the transesterification process, a low density value is indicative of an excessive amount of alcohol (León et al., 2009). The average values obtained in the research were found to be in the range of the European Standard EN 14214 (Min: 0.860 g/mL, Max: 0.900 g/mL), Brazilian Standard (0.850 to 0.900 g/mL).

Table 3: Density in biofuel sample at 25°C and 40°C

Sample	Pycnometer mass (g)	Pycnometer + biofuel mass (g)	Density at 25°C (g/mL)	Density at 40°C (g/mL)
M1	38.4810	83.8809	0.9080	(g/mL)
M2	38.3628	83.6595	0.9059	0.9007
M3	37.2840	82.7197	0.9087	0.9000
		Average	0.9075	0.8990

Table 4: Falling time of water and biofuel in Ostwald viscometer

Sample	Drop time			
	Distilled water		Biofuel	
	25 °C	40 °C	25 °C	40 °C
M1	2.71"	2.5"	12.21"	8.88"
M2	2.77"	2.4"	12.43"	8.31"
M3	2.73"	2.3"	12.32"	8.31"
Average		2.4"	12.32"	8.5"

3.4 Biofuel kinematic viscosity

It is necessary to know the dynamic viscosity. The Ostwald viscometer is used to measure the falling time of distilled water solutions and the biofuel sample at 25 °C and 40 °C. The results are shown in Table 4. The determination of the dynamic viscosity is carried out considering the Eq (2).

$$\mu_{sol} = \frac{\rho_{sol} * t_{sol} * \mu_w}{\rho_w * t_w} \quad (2)$$

Where:

μ_{sol}: Viscosity of the test solution at 40 °C; μw: Viscosity of distilled water at 40 °C. (0.6532 cP); ρsol: Density of the test solution at 40°C; ρw: Density of the distilled water at 40°C (0.992 g/mL); tsol: Time taken to pass through the two marks of the test solution at 40 °C; tw: Time taken to pass through the two marks of the distilled water at 40 °C. In Eq (2) we obtain: for sample M1 it was 2.192 cP, for M2 it was 2.051 cP and for M3 it was 2.051 cP. The average dynamic viscosity of the three samples subjected to 40°C is 2.098 cP.

The kinematic viscosity is calculated using Eq (3):

$$v = \frac{\mu}{\rho} \quad (3)$$

Where: v : Kinematic viscosity; μ : Dynamic viscosity; ρ : Density

Replacing it gives the following kinematic viscosity result at 40°C:

$v_{(40°C)}$ = (2,098 cP)/(0,8999 g/mL) = 2,3314 cSt = 2.3314 mm²/s

The kinematic viscosity at 40 °C for biodiesel (B100), according to the Technical Specifications of NTP 321.125:2019 - second edition, indicates the value of 1.9 to 6.0 mm^2/s using the AST D 445 test method; therefore, the value found in Macrocystis pyrifera biofuel is within the values required by the Peruvian standard.

3.5 Calorific Potential

The ASTM D240 standard method allows the evaluation of the calorific value of fuels, which consists of burning a sample in an oxygen calorimetric pump, observing the temperature before and after combustion. Scientific literature indicates that for renewable fuels the Upper Calorific Value (HCP) should be between 40 to 55 and Lower Calorific Value (LCP) between 43 and 49, in the case of non-renewable fuels (Escalante, et al. 2011). For the research, according to the laboratory report of the National Agrarian University where the Calorific Potential test of samples of *Macrocystis pyrifera* algae was carried out, 39.43 MJ/kg was obtained for the HCP and 39.40 MJ/kg for the LCP, these values are very close to the LCP and HCP values of the methyl ester (Escalante, et al. 2011), being suitable for use especially in machines of lower power.

3.6 Other characteristics of biofuel from *Macrocystis pyrifera* algae

Table 5 shows the results of the analysis of the biofuel obtained from Macrocystis pyrifera, which when compared with NTP 321.125.2019, it is established that it complies with the quality established in Peruvian and other international standards such as EN 14214, ASTM d6751 and the ANP.

Table 5: Results of analysis of Macrocystis pyrifera biofuel.

Tests performed	Units	For biofuel from Macrocystis pyrifera	Specifications			
			EN 14214	ASTM D6751	ANP N°7/08	NTP 321.125.2008
Acid Number	mg KOH/g	0.344	0.5	0.5	0.5	0.5
Carbon Residue (Conradson)	% (m/m)	0.024	0.3	0.05	0.05	0.05
Sulfated Ash	% (m/m)	0.017	0.02	0.02	0.02	0.02
Density	g/mL	0.8999	0.86 – 0.9	-	(20°C) 0.85 – 0.9	-
Viscosity	cSt (mm^2/s)	2.3314	3.5 – 5.0	1.9 – 6.0	3.5 – 6.0	1.9 – 6.0

4. Conclusion

The benthic flora of marine algae Macrocystis pyrifera is a biomass from which quality biofuel can be obtained with characteristics that meet the Peruvian Technical Standard NTP 321.125.2019 and other international standards for fuels; it also has a superior calorific potential (HCP) of 39.43 MJ/kg and a lower calorific potential (LCP) of 39.40 MJ/kg, very similar to biofuels from methyl esters. This biofuel represents a viable alternative with advantages for the conservation of the environment by emitting low pollutants, representing a solution to the energy shortage and future change of the energy matrix to renewable energy sources.

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