

## An Innovative Biodiesel Production

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The production of energy from renewable and waste materials is an attractive alternative to the conventional agricultural feed stocks. This paper describes an approach to extract oil from marine algae and to convert it into biodiesel. The amount of oil in the algae source varies from 0.5 to 3.0 wt % depending its types This process yields 10-15% oil depending on the algae species. The obtained biodiesel (100% conversion of oil to biodiesel) .....

### 1. Introduction

Biodiesel is an alternative biofuel produced by chemically reacting a vegetable oil or animal fat with a short-chain alcohol, such as methanol, ethanol, or butanol and a catalyst (Meher et al., 2006). Biodiesel is obtained from vegetable oils and animal fats (Marchetti et al., 2007), so it is an important tool for combating environmental degradation because of its ecofriendly nature, liquid nature, and easy portability (Balat, 2007; Beer et al., 2002). However, a global debate has now emerged because this fuel is derived primarily from soybean oil or other cereals and using food to produce fuel is not reasonable considering the increase in world population.

In order to solve this problem, industries use waste vegetable oil and grease and animal fats from poultry to produce biodiesel (Nebel and Mittelbach, 2006; Phan and Phan, 2008). In addition, researchers are developing certain crops with high oil content just for the production of biodiesel (Cardone, et al., 2003; Gressel, 2008) or looking for new sources to produce biodiesel (Kondamudi, et al., 2008).

Therefore, it would be very useful to look for new raw sustainable materials for biodiesel production that do not involve the use of cereals. In this work, an innovative biodiesel production from Galician marine algae has been carried out. The use of this raw material can give a solution from an environmental and economic point of view.

Galicia (north eastern Spain) has 35% of the total Spanish coastline. It is a region with an abundance and wide diversity of marine species and has a deeply-rooted seafaring tradition. Algae in Galicia have been traditionally used for agricultural uses. Coastal residents have always collected upon arrival at the coast after storms, to use such as fertilizer, correcting the soil pH, and even as food for livestock. And Galicians have also used seaweed for their own consumption in times of great famine.

There are a great number of different marine algae but only some species are being used as a food product. The other species are collected in the beaches and they are treated as a waste. Then, we have focused the biodiesel production from algae that do not have any use. In this paper, a brief description on the extraction, transesterification, and purification process to produce biodiesel from marine alga is reported.

## 2. Materials and Methods

### 2.1 Materials

Different type of marine algae (*Fucus Spiralis*, *Saccorhiza Polyschides*, *Sargassum Muticum*, *Codium Tomentosum*, *Ulva Rigida*, *Enteromorpha Intestinalis*, *Ascophyllum Nodosum*, *Pelvetia Canaliculata*) were collected from the Galician beaches, washed with water and sun-dried for a few days, since water inhibits transesterification. After that, the dried algae were crush in two steps in order to obtain small solid particles.

Fatty acid methyl esters, anhydrous methanol (ACS grade), sodium hydroxide (98%), n-hexane (ACS grade) were supplied by Panreac.

### 2.2 Oil Extraction

Three hundred mL of n-hexane was used for 40-60 g of dried algae, depending on the algae type, for the oil extraction. The extraction was carried out in a Soxhlet apparatus for 4 h according to UNE-EN 734-1 (2006). The extraction was carried out in order to determine the algae oil content.

All of the experiments were carried out using a 0.5 L round-bottomed glass flask. The resultant solution was separated from solvent by distillation. The solvent was reused in the next batch of extraction. Finally, the sample was dried in an oven (100 °C) until constant weight.

### 2.3 Transesterification Process

The transesterification process was conducted simultaneously with the extraction in order to avoid the previous step of oil extraction and purification of obtained oil. Then, 100 g of dry algae was mixed with 300 mL of hexane and introduced in a thermostated reactor. The mixture was heated at 62 °C and after that, methanol (10 wt % dry basis) in which sodium hydroxide (0.1 wt% dry basis) had been previously dissolved was added to the reactor. Reaction was conducted at the same temperature for four hours with constant stirring at 110 rpm. The reaction mixture, after the reaction, was cooled to room temperature. Then, the solid phase was separated by filtration using a Buckner funnel under vacuum. Finally, the bottom layer of glycerin was separated from the mixture biodiesel and hexane layer (top layer), which was then washed with water to remove the methanol excess and the traces of catalyst (Karaosmanoglu et al., 1996; Lang et al., 2001). In order to obtain the crude biodiesel was necessary to remove the solvent by distillation. The solvent was reused in the next batch of reaction.

### 2.4 Analysis of fatty acid methyl esters

The linolenic acid methyl ester content was quantified using a gas chromatograph Trace GC-Ultra connected to an Innovax capillary column (60m x 0.25mm x 0.25µm), from Agilent Technologies. The temperature program was as follows: 50 °C for 2 min and raised to 240 °C at a rate of 10 °C/min and maintained for 27 min. The injector was set

up for 240 °C and the FID detector at 220 °C. Helium was used as carrier gas, at constant flow of 1 mL/min.

The analysis was carried out by diluting the biodiesel (diluted to 1  $\mu$ L by adding 1000  $\mu$ L of hexane), and 0.5  $\mu$ L of this solution was injected through the column. Nonanoic acid methyl ester was used as an internal standard.

### 3. Results and Discussion

This work has been divided in two main sections. The first step on this research consisted of algae characterization in order to determine the best type to carry out the transesterification process. Once algae were characterized, the reaction was carried out simultaneously with the oil extraction with the aim of optimizing the process.

#### 3.1 Algae characterization

Eight types of algae collected from Galician coast were analyzed in order to determine the oil content using n-hexane to carry out the extraction. It was observed that these algae do not have a very high oil content (Fig. 1), therefore it will be necessary to use a great amount of raw material in order to obtain the biodiesel. This could seem an inconvenient; however only at south of Galicia more than 1500 tonnes/year are collected from the beaches.

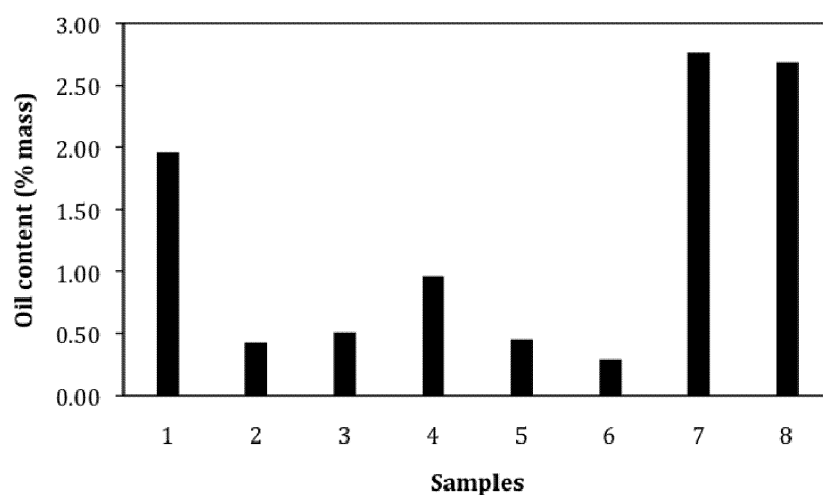


Figure 1. Oil content of the different type of algae: 1 *Fucus Spiralis*; 2 *Saccorhiza Polyschides*; 3 *Sargassum Muticum*; 4 *Codium Tomentosum*; 5 *Ulva Rigida*; 6 *Enteromorpha Intestinalis*; 7 *Ascophyllum Nodosum*; 8 *Pelvetia Canaliculata*.

Considering that most of the types have a lower content, the algae were mixed in order to obtain a homogeneous value for oil content. Moreover, the algae are mixed when they are collected from the beaches. Three different mixtures were obtained and their oil content was also determined by extraction with n-hexane. The oil content of the three mixtures is showed in table 1.

The composition of algae mixture was the following:

MIX 1: *Fucus Spiralis*, *Sargassum Muticum*, *Codium Tomentosum*, *Ulva Rigida*, *Ascophyllum Nodosum*, *Himantalia Elongata*.

MIX 2: *Fucus Spiralis*, *Sargassum Muticum*, *Codium Tomentosum*, *Ulva Rigida*, *Ascophyllum Nodosum*, *Himantalia Elongata*, *Cryptopleura Ramosa*, *Undaria Pinnatifida*, *Padina Pavonia*.

MIX 3: *Enteromorpha Intestinalis*, *Ulva Rigida*.

Table 1. % oil content of the different samples.

SAMPLE	% OIL
MIX 1	1.26
MIX 2	0.65
MIX 3	0.31

### 3.2 Transesterification Process

Extraction and transesterification of extracted oil to biodiesel was carried out simultaneously. In order to check the viability of the simultaneous process, a sample of algae were undergone to Soxhlet extraction with n-hexane, as described for determining the oil content of algae, after the completion of reaction and it was observed that the most algae content had been extracted during the reaction (more than 75%).

Finally, the conversion of oil to biodiesel was determined for each sample. As expected, the maximum oil to biodiesel transformation was observed in mixture 1 which the most oil content (Fig. 2). Then, it can be said that the conversion of oil to biodiesel is very high.

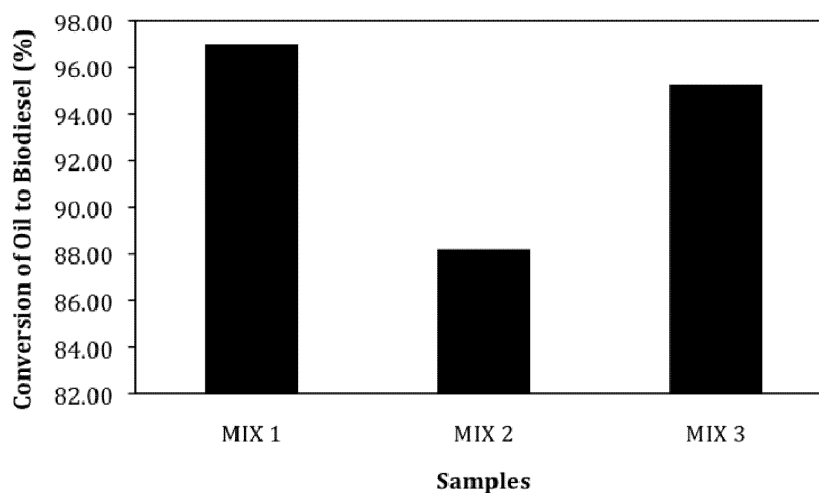


Figure 2. Conversion of oil from algae to biodiesel of the different samples.

Finally, the linolenic acid methyl ester content was determined by gas chromatography. It was observed a great variation among the samples (Fig. 3), that could be due to the

different type of algae oil. Although all of them have values lower than 12%, in accordance with the specifications reported in UNE-EN 14214 (2003).

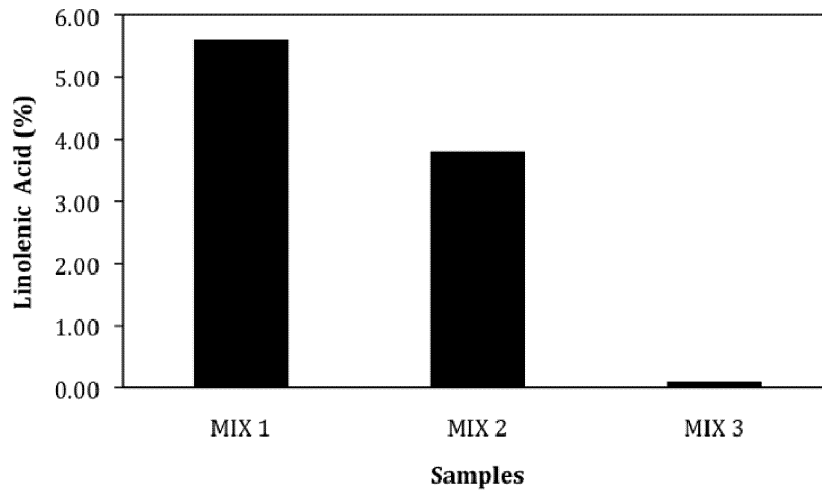


Figure 3. Linolenic acid methyl ester content of biodiesel of the different samples.

In conclusion, it has been demonstrated that marine algae could be used as a source to produce biodiesel so about 75% of the oil obtained from algae was converted to biodiesel with more that 90% yield.

#### 4. Conclusions

Biodiesel production from oil extracted from marine algae is feasible by transesterification. Moreover, this study indicates that the oil extraction can be carried out simultaneously with the transesterification.

Finally, the authors of this work consider that algae biodiesel stocks may become in the future a very attractive investment due to the technique positive points related to the technology.

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