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BIODIESEL PRODUCTION FROM MACROALGAE - CLADOPHORA GLOMERATA

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Abstract: The increasing global demand for energy and stronger environmental concerns have made necessary the search for new and sustainable sources of energy. The use of biofuels,especially in the transport sector, has proved to be an option to reduce the use of oil. Biodiesel represents the 33 % of global biofuel production. Algae can become a suitable source of biomass for biofuels production. Macroalgae, which are multicellular organisms that grow in fresh or salt wáter. Macroalgae are a promising source for biofuel production, they do not compete with the production of food and unlike oil crops, do not require agricultural land for cultivation, pesticides or herbicides. The fatty acids of Cladophora glomerata biodiesel were determined using gas liquid chromatography.

Key words: Macroalgae Cladophora glomerata, Lipid, Biodiesel.

I. INTRODUCTION

Macroalgae are normally cultured in freshwater ponds, brackish or seawater, even sewage, where they can consume nutrients from the wastewater to grow and develop. Moreover, macroalgae can fix CO_2 with a photosynthetic efficiency of 6-8 %, unlike terrestrial biomass which has an efficiency of 1.8 to 2.2 % [1]. The search for oil sources that do not occupy arable-land has presented macroalgae as a promising feedstock for biofuels. Biofuel obtained from macroalgae has an important potential [2-3]. The average photosynthetic efficiency of macroalgae is 6–8%, which is much higher than that of terrestrial biomass (1.8–2.2%) [4]. Macroalgae are fast growing marine and freshwater plants that can grow to considerable size (up to 60 min length). Moreover, many species of macroalgae -have not been studied. So, more macroalgae with bigger oil content could be found and, improving farming methods, they could become a viable source for biodiesel production.

Properties of biodiesel:

Biodiesel fuel properties are determined by: 1) The production process, which must be performed correctly and 2) The structure of its component fatty esters which depends directly onthe raw material used for the production. With respect to its relation with the biodiesel composition, the longer thefatty acid carbon chains and the more saturated the molecules, the higher the cetane number [5]. Moreover, fatty acid methyl esters (FAMEs) have slightly lower cetane number than their corresponding fatty acid ethyl esters (FAEEs) [6-7].

II. MATERIALS AND METHODS

1. Extraction of lipid from macroalgae-Cladophora glomerata (chlorophyceae)

The green-filamentous macroalgae Cladophora glomerata was collected & washed with distilled water in order to remove all the dust and sun-dried for 24 Hrs, dried in oven for 3 h at 100 °C. This dried macroalgae biomass was crushed and oil was extracted through the Soxhlet method [8]. The oil extraction was carried out using a round-bottomed flask coupled to a Soxhlet extractor and a condenser, as well as a proportion of 10 mL of n-hexane for mach one gram of dried biomass, 3 Hrs was the oil extraction time. The residual mix of n-hexane-oil was removed under vacuum at 335 mbar, 40°C steam, 15°C of cooling water and a thermostatic bath at 60°C in a rotary evaporator. After a set of extraction, the solvent was recovered and reused for the next extraction batch.

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2. Composition characterization of fatty acids and natural products

The oil obtained from Cladophora glomerata was treated to convert all fatty acid components into the methyl esters for an easier determination.

For the esterification step the oil was heated to 60°C with stirring at 600 rpm, p-toluenesulfonic acid (mass ratio oil − p-toluenesulfonic acid, 200:1) solved in methanol (molar ratio of methanol−oil, 6:1) was added to the reactor, and the reaction mixture was kept at 60 °C with stirring at 600 rpm for 4 h. At the end of the reaction, fresh calcium oxide (mass ratio oil−calcium oxide, 50:1) was added to the reactor at 60 °C with stirring, to neutralize the acid catalyst and to eliminate the water produced in the esterification, forming insoluble calcium hydroxide.
In the transesterification process, the mixture of oil and methanol from the esterification process was heated to 60 °C stirring at 600 rpm. Sodium methoxide (mass ratio oil−sodium ethoxide, 100:2) dissolved in methanol (molar ratio of methanol−oil, 6:1) was added to the reaction mixture. After 3 h, the reaction mixture was cooled to room temperature. Later decanted in the centrifuge tubes and centrifuged at 3000rpm for 5 min, and the upper biodiesel phase was separated from the lower phase. Thefatty esters were transferred to a rotary evaporator to eliminate the methanol excess, treated with 2 wt % Magnesol at 77 °C, stirring at 800 rpm for 30 min, and filtered through a 0.5 μm filter.
The fatty acid profile of the sample was determined using a gas chromatograph equipped with flame ionization detector (FID) and split/splitless injector. Methyl heptadecanoate in heptane (5 mg/mL) was used as standered. Sample preparation: 250 mg of sample dissolved in 5 mL of methyl heptadecanoate solution. A gas chromatography coupled to a mass spectrometer was used. Helium was used as the carrier gas. The injector temperature was 250 °C and the column temperature of each run was started at 50 °C for 3 min, then raised to 310 °C at 10 °C/min and maintained at 310 °C for 10 min.

III. RESULTS AND DISCUSSION

1. Lipid extraction and methylester fatty acid characterization

The initial humidity content for Cladophora glomerata macroalgae was 58%, and was reduced to 0.3 % after being dried in the oven. The oil content obtained using Soxhlet extraction method was 4.0mL/40 g, achieving a total oil content of 65 mL from dried biomass. The oil yield was 2.0 %. The oil content obtained in this thesis is between the limits reported previously for macroalgae, 1.3 and 7.8 wt % [9]. Some examples are Cladophora, 2.48 %; Gracilaria, 2.01 % and Spirogyra, 3.01 % as reported. [10]]. The fatty acid composition of the Cladophora glomerata oil, analyzed by GC, is shown in Table 3. It showed higher saturated fatty acids compared to unsaturated fatty acids. The most common saturated fatty acid in algal cells is the palmitic acid constituting35-40 % of total fatty acids. However, red and brown algae, have lower levels of C_{20} andC_{22} polyunsaturated fatty acids, while the green algae contain high levels of C_{16} and C_{18} polyunsaturated fatty acids [11]. The concentration of light fatty acids is high compared to most of vegetable oils, and especially that of palmitoleic acid. Also, theiodine value is not so high (95 g I_2/100 g oil) because the content in linoleic acid is much lower than that usually found in vegetable oils. The analysis made with GC-MS permitted to identify other compounds than fatty acids, as shown in Figure 1. The chromatogram showed a high percentage of natural products (45%). In addition, other products such as squalene, cholesterol and neophytadiene reported lower percentages. The sample has significant hydrocarbon content (20%), between C17 and C29. These hydrocarbons with odd number of carbons are produced by decarboxylation of fatty acids caused by an enzyme recently found in algae [12]. This is important because hydrocarbons are a source of energy used worldwide, as components of petroleum and natural gas.

Table 1: Fatty acid compositions of Cladophora glomerata oil (%):

Fatty acid	Cladophora glomerata
Caprilic	-
Lauric	6.18
Myristic	3.6
Palmitic	38
Palmitoleic	5.04
Stearic	4.58
Oleic	2.31
Linoleic	12
Linolenic	7.03

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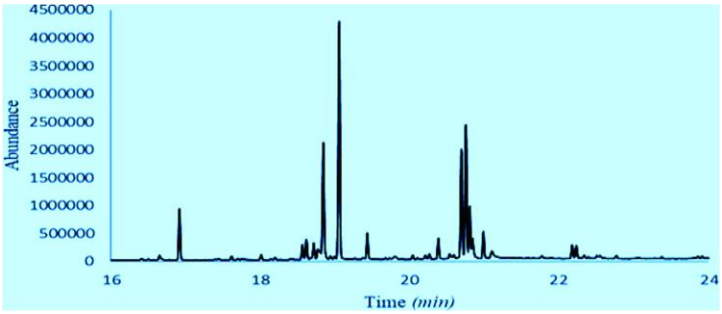
Eicosatrienoic	-
Eicosatetraenoic	-
Behenic	8.27
Others	7.46

Fig.1: Chromatogram of GC-MS of FAME Cladophora glomerata oil



Physicochemical characterization

The Cladophora glomerata macroalgae oil viscosity at 40 °C (mm^2/s) measured by Viscosity meter is less (0.6) compared to other algae and vegetable oils [13-14]. This oil is not used directly as diesel engine fuel but is used as used as an additive to decrease the viscosity when blended with other oils. Heating value which is analyzed by Calorimeter is also higher than other macroalgae oils [15-16] a higher heating value of Cladophora glomerata oil is used as an additive for other oils. About the elemental composition (carbon, hydrogen and nitrogen) analyzed by Elemental Analizer where carbon percentage 41(% m/m). The hydrogen content is 15(% m/m), nitrogen content is 0.06 (% m/m). Results of elemental composition can be related to the environmental conditions during its growth cycle, biochemical composition changes or the presence of natural compounds.

CONCLUSIONS

Cladophora glomerata can be used for production of liquid biofuel. The macroalgae showed low lipid content when compared to marine macroalgae.

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