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Macro Green Algae (Chlorophyta) Biodiesel Energy Liquid Fuel Synthesis by Single-Step In-situ Transesterification Method

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Abstract: ***The present paper was emphases on study of macro green algae from Ahmednagar district of Maharashtra State, India. The macro alga was innovative and very interesting aquatic biomass source for making the energy liquid biodiesel fuel. Algae have a higher photosynthetic activity with respect to terrestrial plants. It was adapt in various growing condition either fresh or marine water without acquiring the land. The collection of macro algae were quite easy than the microalgae. The harvesting and drying processes were play vital role in converting algal biomass into energy liquid fuel. The oil extraction was the important step for the biodiesel synthesis. This step was skipped and algal biomasses directly convert to fatty acid methyl ester by In-situ transesterification method. The single step method can be attractive solution to reduce the chemical like hexane and energy consumption in the overall biodiesel production and eco-friendly. The characterization of obtained product was done by standard analytical methods. The functional group present in product components was studied by FT-IR spectroscopy and its separation with the help of Gas Chromatography Mass Spectroscopy. The product comprises mixture of seven types of fatty acid methyl ester with different retention time and concentration.***

Keywords: Macro algae, In-situ Transesterification, Biodiesel, FT-IR spectroscopy, GC-MS.

1. Introduction

Energy is primary requirement for the innovative activity and attractive life style of human. The basic energy sources are fossil fuel. The energy demand increases continuously due to increasing population and industrialization. The world may face the challenges like scarcity of fossil fuel, rising price of petroleum based fuel, deforestation and growing global warming. Hence the researchers have seriously focused on the renewable energy sources as key solution for replacement of fossil fuel [11] [15]. The renewable energy is obtained from various sources like agriculture, forestry and aquatic. These sources are taken in consideration as good feedstock producer for making the biofuel such as biodiesel, bioethanol, bio-oil and biogas [3] [28]. Hence, the utilization of renewable biomass energy in large extent provides sustainable development which link to global stability, economic balance, innovation in local market, reduces green house emission and quality of life [30].

Algae are a diverse group of prokaryotic and eukaryotic organisms ranging from unicellular to multicellular forms [21]. Algae can be growing in an autotrophic or heterotrophic condition. The autotrophic algae require only inorganic compounds such as CO_2, salts and light energy source for their growth, while the heterotrophic are non-photosynthetic, which require external source of organic compounds and nutrients as energy sources [4]. The algae have ability to grow throughout the year; therefore, algal oil productivity is higher in comparison to the conventional oil seed crops. In algae cultivation the rate of water consumption is low and it does not require pest controller compounds. The algae possessing short harvesting cycle than the conventional crop cycle, hence it is better advantage to carry out the algal biomass as biofuel [7] [10] [29].

Macro-algae are member of huge group of multicellular plant. It derives their entire nutrient directly from surrounding water through their tissue. There are various types of macro-algae like green algae (Chlorophyta and Streptophyta), red algae (Rhodophyta), brown algae (Phaeophyceae) and yellow-green algae (Xanthophyceae) [17] [20]. Macro-algae have several potential advantages as compare to terrestrial plants for the sustainable production of biofuels [19]. Macro-algae does not require agriculture land and fresh water to grow and productivity of some microalgal species can be high [5] [13] [22] [24]. The chemical compounds in macro-algae can be used as food, fodder or chemistry industry and biofuel production [6] [13] [14]. After the fuel conversion of macro-algae, the remaining biomass can be used as a fertilizer, for heating, or as substrate to produce another type of biofuel [14] [23] [25] [31].

2. Materials and Method

2.1 Collection and Identification of Macro-algae

The Macro-algae which floating on water was collected from fresh water Godawari River is situated at Kopargao city in Ahemdnagar District, Maharashtra, India. The collection of macroalge is quite easy by possible to install net when it risen water run-off. This step require less energy for macro-algae than microalgae because need of filtration for the separation. Algal sample were observed under the compound microscope and identified with the help of standard literature.

2.2 Drying of the Macro green Algae

The Sun-drying is the important method for drying of macrophytes [2] [12] [31]. This method save the fossil fuel but it depends on climatic condition and volume of biomass. Sun-drying in tropical region may take 2-3 days in sunny weather and may take up to 7 days in rainy seasons [4].

2.3 Biodiesel synthesis by In-situ Transesterification Method

The "In-situ transesterification" is "reactive extraction" process for synthesis of fatty acid methyl ester. Biodiesel content obtained from algae powder without extraction of oil. The alcohol acts as an extraction solvent and extraction reagent which enhance the product yield. These reactions are often catalyzed by the addition of an acid or base catalyst. Transesterification is three steps reaction while In-situ transerification is one step reaction (Figure 1), there is oil extraction step skips hence saving the solvent like hexane as well as reduce the atmospheric pollution and global warming [26]. According to Hass and Wagner (2011) [18], In-situ transesterification method has high heating value with higher product yield. It is quick and simple operation process without loss of lipid. This method reduces the process cost due saving solvent, absence of extraction process and it reduce the waste water pollutants.

The base catalyzed reaction according to Dalvi et al. (2012) [8]and methanolic KOH catalyst used. The mixture of KOH and MeOH was added in round bottom containing dried macro-algae powder. The reaction mixture was continuously stirring. The reaction carried out at 60˚C for 60 minute. At room temperature reactions mixture was cooled and separates the algal remnant and product. The product was wash water to remove water soluble impurities [32] and heat the product at 85˚C. The fatty acid methyl esters were analyzed by standard method Infrared spectroscopy and gas chromatography mass spectroscopy.

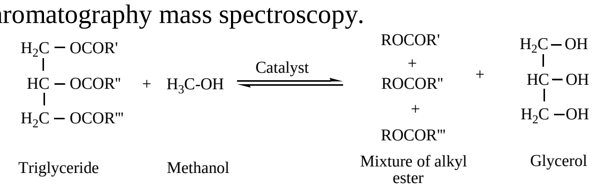

Figure 1: Transesterification reaction of the Triglyceride.

3. Results and Discussion

3.1Characterixation of Isolated Algae Sample

The isolated algae were belonging from the division of Chlorophyta. The order of Volvocales, Tetrasporales, Chlorococcales, Chlorosacinales, Ulotriches, Sphaeropleales, Cheatophorales, Trentopohiales, Oedogoniales and Ulvales species were observed.

3.2 Infrared Spectroscopy Analysis

The IR Spectroscopy is the method to determine the function group present in the obtained product. The macro-algae fatty acid methyl esters are analyzed by infrared spectroscopic method (Figure 2). Infrared Spectrum of Base catalyzed In-situ transesterification of Macro-algae Biodiesel shows the υ_{as} (sp^3 C-H) stretching of ester group of fatty acid methyl ester at 2925.51 cm^{-1} , υ (C=O) stretching of ester at 1743.63 cm^{-1} , δ_s (CH_2) bending of methylene group at 1461.94 cm^{-1} , δ_s (CH_3) bending of methyl group absorption frequency at 1373.22 cm^{-1}, υ (C-O) stretching of alkyl carbon and oxygen from fatty acid methyl ester at 1170.71 cm^{-1}, δ_r (CH_2) bending of methylene group was observed at 726.10 cm^{-1}.

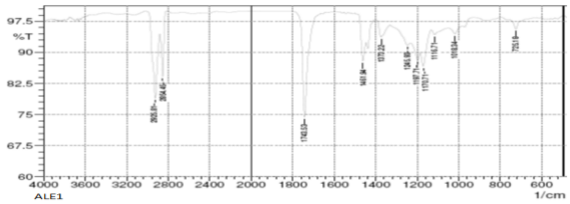

Figure 2: FT-IR Spectrum of Macro-algae Biodiesel

3.3 Gas Chromatography Mass Spectroscopy Analysis

Gas chromatography mass spectroscopy is used to separate and identify the chemical ingredients in the biodiesel. The Figure 3 shows Gas chromatographic spectrum with the various peak obtained at different retention time. In Base catalyzed Biodiesel of Macro-algae, seven types of ester obtained at retention time (min) at 12.486, 14.952, 17.071, 17.190, 18.922, 18.976 and 19.201. Mass spectrum fatty acid methyl ester of energy liquid fuel shown in figure 4, 5, 6, 7, 8, 9 and 10 respectively. The four components of biodiesel at retention time (min.) 12.486, 14.952, 17.190 and 19.201 shows the base peak at m/z 74.05 [Figure 4, 5, 7, 10]; the two components at 17.071 and 18.976 min. shows base peak at m/z 55 [Figure 6, 9], while one component at 18.922 shows the base peak at m/z 67 [Figure 8]. The experimental test results and the ester were confirmed with MS library. Table 1 shows the peak obtained with various retention times, percentage area, name of the obtained compound and molecular formula.

The Macro-Green Algae Biodiesel contain higher content of Hexadecanoic acid methyl ester (29.15%), 9-Octadecenoic acid (Z) methyl ester (18.63%), 9, 12-Octadecadienoic acid(Z,Z) methyl ester (8.12%) and in small content of Tetradecanoic acid methyl ester (4.94%), 9-Hexadecenoic acid methyl ester (4.23%), Octadecanoic acid methyl ester (4.04%), Dodecanoic acid methyl ester (1.01%).

4. Conclusions

The present paper was study the macro green algae Chlorophyta species found in Ahmednagar district of Maharashtra State, India. The biodiesel energy liquid fuel of macro green algae was synthesis by In-situ transesterification Method. The obtained product biodiesel liquid fuel is characterized by FT-IR Spectroscopy and Gas Chromatography Mass Spectroscopy. The FT-IR shows the characteristic peak of ester at 1743.63 cm^{-1}. The component of biodiesel separated by Gas Chromatography and identify with standard data MS library. The base catalyzed biodiesel of macro algae biodiesel contain mixture of 30.98% unsaturated fatty acid methyl ester and 38.24% saturated fatty acid methyl ester. The fatty acid obtained was ranging between C13 to C19.

The macro-algae is a challenging material for biodiesel production due to its higher content of polyunsaturated fatty acids and unsaturated fatty acids [1] [9] [16], But the best solution to decrease polyunsaturated fatty acid is drying [27]. The GC-MS study (Figure 3) state that the biodiesel from macro green algae contains mixture of saturated fatty acid unsaturated fatty acid methyl esters, hence its oxidative stability is higher . Thus, Macro green algae can be considered as potential algae for biodiesel production because of their large availability and easy harvesting. It could be help for innovation in local market, to create job opportunity, sustainability and energy security of the nation.

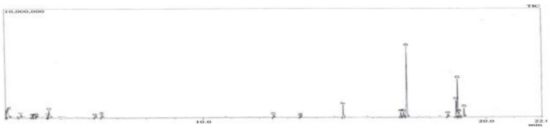

Figure 3: Gas Chromatographic spectrum of Macro-algae Biodiesel.

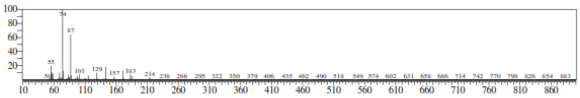

Figure 4: Mass Spectrum of Dodecanoic acid methyl ester

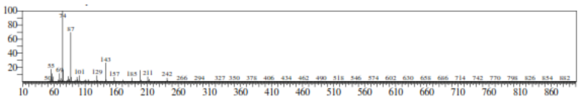

Figure 5: Tetradecanoic acid methyl ester

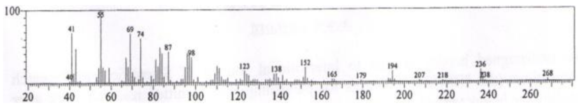

Figure 6: 9-Hexadecenoic acid, methyl ester (Z)

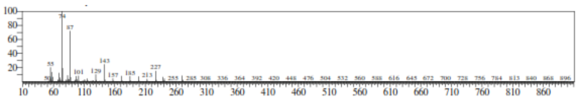

Figure 7: Hexadecanoic acid, methyl ester

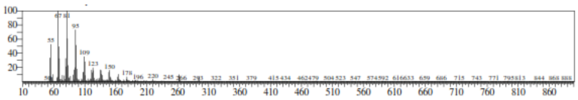

Figure 8: 9, 12-Octadecadienoic acid (Z, Z) methyl ester

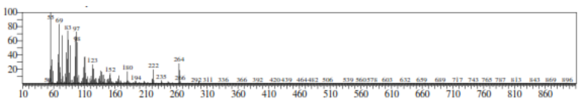

Figure 9: 9-Octadecenoic acid (Z) methyl ester

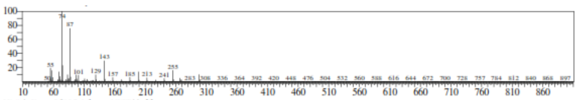

Figure 10: Octadecanoic acid methyl ester

Table 1: Macro-algae Biodiesel Components with Retention time, Percentage area, Name of the Ester Compound and Molecular Formula

Sr. No.	Retention Time (min.)	% Area	Name of the Compound	Molecular Formula
1	12.486	01.01	Dodecanoic acid methyl ester	$C_{13}H_{26}O_2$
2	14.952	04.94	Tetradecanoic acid methyl ester	$C_{15}H_{30}O_2$
3	17.071	04.23	9-Hexadecenoic acid methyl ester	$C_{17}H_{32}O_2$
4	17.190	29.15	Hexadecanoic acid methyl ester	$C_{17}H_{34}O_2$
5	18.922	08.12	9,12-Octadecadienoic acid(Z,Z) methyl ester	$C_{19}H_{34}O_2$
6	18.976	18.63	9-Octadecenoic acid (Z) methyl ester	$C_{19}H_{36}O_2$
7	19.201	04.04	Octadecanoic acid methyl ester	$C_{19}H_{38}O_2$

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