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# Production of algal biodiesel from marine macroalgae *Enteromorpha compressa* by two step process: Optimization and kinetic study

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## HIGHLIGHTS

- *Enteromorpha compressa* is a potential source which has been used for first time.
- Maximum yield of ME 90.6% was achieved by acid–base catalyze transesterification.
- The reaction parameters were optimized and kinetic study was performed in detail.
- The activation energy was obtained as 73,154.89 J/mol.
- Algal biodiesel was characterized and it was within the limits of ASTM standards.

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## ABSTRACT

In this investigation, *Enteromorpha compressa* algal oil with high free fatty acids (FFA) used as a feedstock for biodiesel production. Two step process was developed and kinetic study executed to obtain reaction rate constant for the transesterification reaction. The acid esterification was carried out to reduce FFA from 6.3% to 0.34% with optimized parameters of 1.5% $H_2SO_4$, 12:1 methanol–oil ratio, 400 rpm at 60 °C and 90 min of reaction time. The maximum biodiesel yield 90.6% was achieved from base transesterification through optimum conditions of 1% NaOH, 9:1 methanol–oil ratio, 600 rpm and 60 °C temperature for 70 min. The algal biodiesel was characterized by GC–MS, HPLC and NIR. This transesterification follows first order reaction kinetics and the activation energy was determined as 73,154.89 J/mol. The biodiesel properties were analyzed and found to be within the limits of American standards. Hence, *E. compressa* serves as a valuable renewable raw-material for biodiesel production.



## 1. Introduction

Biodiesel is an excellent substitute for conventional diesel fuel because of being renewable, nontoxic and biodegradable. It consists of mono-alkyl esters usually produced from renewable feedstocks (Demirbas, 2009). At present, the high cost of biodiesel is the major obstacle for its commercialization. Approximately 70–95% of the total cost of biodiesel production is attributed to raw feedstocks (Leung and Guo, 2006; De la Hoz Siegler et al., 2011). The availability of the oil crops serve as the sources for the biodiesel production are limited (Chisti, 2008). Macroalgae are a potential alternative source for the conventional feedstocks (Ross et al., 2008) and algal oil is suitable for esterification/transesterification reaction of biodiesel production. The recent renewable source of algal oil that could meet the global demand for transport fuels.

Only limited investigations have been reported for the biodiesel production from marine macroalgae. Marine macroalgae is a potential biomass for renewable energy. Annual primary production rates of macroalgae biomass are very high when compared to other biomass (Ross et al., 2008). Due to Eutrophication and harmful effects to the environment (Blomster et al., 2002), *Enteromorpha* sp., is used as feedstock for biodiesel production to clean up the detrimental biomass. *Enteromorpha compressa* is a green algae belongs to phylum chlorophyta and ulvaceae family. It is elongated, tubular (although the tubes are often partially compressed), hollow fronds and composed of single layer thick cells (Blomster et al., 2002). It is distributed in Arctic, Ireland, Europe, Atlantic Island, North America, Caribbean Islands, South America, Africa, Indian Ocean Islands, South-west Asia, Asia, South-east Asia, Australia, New Zealand, Pacific Islands, Antarctic and the sub Antarctic islands. *E. Compressa* exhibits a seasonal growth behavior. In India, this species shows the maximum development during the south west monsoon season from June to September in Gulf of Mannar side of the coast line near Mandapam (Umamaheswara Rao, 1970). 0.36 mm growth (in

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length) per day was noticed during the maximum development period. But it will also be available from October to February.

The main objective of this work is to produce biodiesel from *E. compressa* algal oil by conventional methods catalyzed by homogeneous catalyst such as NaOH and $H_2SO_4$. Since algal oil contains high free fatty acids (FFA), when a base homogeneous catalyst is used, FFA reacts with the catalyst to produce emulsified soap that will inhibit biodiesel production. If an acid catalyst is applied, despite the saponification phenomenon is avoided but the acid has a less catalytic effect on the transesterification. Thus causes slower reaction rate leads to longer time reaction and also less efficient method (Deng et al., 2010). Therefore, a two step process, acid esterification using $H_2SO_4$ to remove FFA followed by base transesterification using NaOH, was used for the production of biodiesel from the *E. compressa* algal oil. Later, optimization of the acid pretreatment process for reducing the FFA content of algal oil below 1% for maximum biodiesel production and optimization of the reaction parameters for the base transesterification with methanol using NaOH catalyst was established. No literature was found for the production of biodiesel from marine macroalgae *E. compressa* by two step process.

This paper also focuses on the kinetic study of the transesterification reaction for the production of biodiesel. From this kinetic study, the reaction rate constant and activation energy were determined. Besides, fuel properties of algal biodiesel were analyzed according to the American standard test methods (ASTM D-6571-6). As a result, utilization of marine macroalgae *E. compressa* for biodiesel production, provides dual benefits, it serves as a biomass for the production of biofuels and also save our environment from detrimental effects.

## 2. Methods

### 2.1. Materials

Methanol (99.9% purity), *n*-hexane (99% purity), diethyl ether (99% purity), methylene chloride (99% purity), sulfuric acid (95–97% purity) and sodium hydroxide (99%) were purchased from Merck Ltd., Mumbai, India. All the chemicals used were HPLC grade.

### 2.2. Collection and preparation of algal sample

*E. compressa* was collected from Gulf of Mannar, Mandapam coast, Rameswaram. The samples were thoroughly cleaned in fresh water followed by distilled water, dried in shade condition and in oven at 60–70 °C, pulverized and sieved. The dried algal biomass was used for biodiesel production.

### 2.3. Extraction of algal oil

#### 2.3.1. Pretreatment of algal biomass by ultra – sonication

Dry algal biomass along with water (water to biomass ratio as 3:1 v/w) was taken in a conical flask. Ultra – sonication was carried out using ultrasonic probe at 24 kHz with constant temperature (50 ± 1 °C) for 5 min. After destruction of algal cells, the biomass was dried in shade conditions and in oven at 60 ± 5 °C. The pretreated algal biomass was loaded for effective extraction (Suganya and Renganathan, 2012).

#### 2.3.2. Soxhlet extraction of algal oil

The pretreated *E. compressa* algal powder fed to a Soxhlet extractor fitted with a round bottom flask with condenser. The extraction was executed for 6 h with the solvent system as 1% diethyl ether and 10% methylene chloride in *n*-hexane (Suganya and Renganathan, 2012). The solvent was removed under vacuum at 400 mbar in a rotary evaporator (Eyela, N–N Series, Rikakikai Co. Ltd., Tokyo, Japan). The temperature was maintained at 45 °C.

#### 2.3.3. Determination of physicochemical properties of algal oil

Physical (density, kinematic viscosity and average molecular weight) and chemical (iodine value, acid value, FFA content and saponification value) properties of algal oil were analyzed using the standard procedures (AOCS, 1998; Vicente et al., 2004).

### 2.4. Experimental set up for biodiesel production

A thermostatic stirrer glass reactor at atmospheric pressure was used for acid–base transesterification process and kinetic study. Three trial runs were carried out for each combination of reactants and process conditions.

Acid esterification: Sulfuric acid was used as catalyst for acid-esterification pretreatment to remove the FFA. The flask was filled with algal oil and heated to remove the moisture content. The reaction mixture of concentrated $H_2SO_4$ in appropriate volume of methanol was separately heated at 60 °C and then added to the flask. The mixture was vigorously stirred and refluxed for the required reaction time to complete the esterification. The progress of the reaction was routinely monitored by measuring the acid value and FFA at different temperature and the samples were withdrawn at pre-determined time intervals to calculate acid value. After acid catalyzed esterification, the final reaction mixture was poured into a separating funnel. The upper layer was collected and purified by distilled water wash and measured to calculate the biodiesel yield. The lower layer (oily phase) was separated, washed with distilled water, and then centrifuged to remove excess alcohol, $H_2SO_4$ and impurities. Then the mixture was dried and used for further processing by the base catalyzed transesterification. The esterification parameters which influence the reduction of acid value and FFA were optimized.

Base transesterification: The algal oil produced by the above step was further transesterified into biodiesel catalyzed by NaOH. The pretreated algal oil was poured into the reaction flask and heated. Simultaneously, the NaOH was dispersed and dissolved in methanol and then added with the esterified algal oil. The reaction mixture was stirred at different temperature for 90 min using a magnetic stirrer. The samples were withdrawn from the reaction mixture during the progress at pre-determined time intervals to find out the yield of ME. After 90 min, the reaction mixture was poured into a separating funnel and allowed to separate into two layers. The upper phase consists of ME and the lower layer contains glycerol with other impurities. The lower layer was discarded. The upper ME layer was collected and further purified by washing with hot distilled water three times. Residual water was then removed and methyl esters layer was dried using sodium sulfate, followed by filtration using Whatman filter paper No.42. The final purified biodiesel was taken for GC–MS, HPLC and NIR analysis and fuel properties examination.

The yield of methyl esters was calculated using the following formula (Rashid et al., 2010) (Eq. (1)):

$$\text{Yield of methyl esters}\,(\%) = \frac{\text{grams of methyl esters produced}}{\text{grams of oil used in reaction}} \times 100 \quad (1)$$

In this process, the reaction parameters such as catalyst concentrations, methanol to algal oil ratios, mixing intensity and reaction temperature were used to investigate their effects on biodiesel yield.