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TRANSESTERIFICATION OF ALGAL OIL USING NANO CaO CATALYST

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ABSTRACT

Biodiesel is considered as one of the prime sources of non conventional transportation fuels. Though there are various sources available for biodiesel production, algal oil holds importance since it is non-edible and abundantly available. In this study, we carried out transesterification of oil extracted from marine algae using nano calcium oxide catalyst. Nano calcium oxide catalyst was produced by calcinating clam shell powder. Algae biomass were collected from coastal areas near Chennai, dried, crushed and sieved for uniform sized particles. Transesterification experiments were carried out using extracted oil from algal biomass using hexane as a solvent. Effects of oil to methanol ratio, temperature and catalyst loading were analyzed and the optimum values were determined. FAME analysis was done to qualify and quantify the biodiesel yield. Experimental results showed that algal oil is a good source of oil and nano CaO catalyst is an effective catalyst for transesterification.

Key words: Algae oil, Transesterification, Biodiesel, Nano CaO catalyst, FAME analysis.

INTRODUCTION

The negative impacts of global warming, now accepted as a serious problem by many people, have clearly been observed for past decade and seems to intensify every year. The release of the carbon oxides and related inorganic oxides are more than the amount that could be absorbed by the natural sinks in the world since 88% of the world energy demand is provided by carbon based nonrenewable fuels[1]. It is vital to develop solutions to prevent and/or reduce the emission of greenhouse gases, such as carbon dioxide, to the atmosphere. Carbon dioxide neutral fuels like biodiesel could replace fossil fuels.

Biodiesel seem to be a viable choice but its most significant drawback is the cost of crop oils, such as canola oil, that accounts for 80% of total operating cost, used to produce

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biodiesel[2]. Besides, the availability of the oil crop for the biodiesel production is limited[3]. Therefore, it is necessary to find new feedstock suitable for biodiesel production, which does not drain on the edible vegetable oil supply. One alternative to oil crops is the algae because they contain lipids suitable for esterification/transesterification. Among many types of algae, algae seem to be promising because:

(i) They have high growth rates e.g., doubling in 24 h[4].

(ii) Their lipid content could be adjusted through changing growth medium composition[5].

(iii) They could be harvested more than once in a year[6].

(iv) Salty or waste water could be used[6].

(v) Atmospheric carbon dioxide is the carbon source for growth of microalgae[6].

(vi) Biodiesel from algal lipid is non-toxic and highly biodegradable[6].

(vii) Microalgae produce 15-300 times more oil for biodiesel production than traditional crops on an area basis[7].

Miao and Wu[8] reported that it was possible to heterotrophically grow microalgae, Chlorella protothecoides; hence resulting in an increase of 55% in the lipid content and also the algal lipid could be transformed into biodiesel with sulfuric acid transesterification under 1 : 1 weight ratio of acid to lipid and 56 : 1 molar ratio of methanol to lipid at 30^{o}C.

In addition, Li et al.[9] showed that it was feasible to grow microalgae, *C. protothecoides*, in a commercial scale bioreactor and also using 75% immobilized lipase, they claimed that 98.15% conversion could be obtained in 12 h when the reaction condition with respect to solvent type, water content, pH was optimized.

On the other hand, Hossain et al.[10] studied biodiesel production from algal oils of macroalgae species Oedigonium and Spirogyra using sodium hydroxide as the catalyst and reported that it was possible to produce biodiesel using even low lipid containing macroalgae. Although there are few studies focused on biodiesel production from different algae species using homogeneous catalysts, such as NaOH and sulfuric acid, there are no studies on the biodiesel production from Algae species using heterogeneous catalysts in the literature. No one has reported the use of clam shell as catalyst in the transesterification

reaction as such the present paper aims to characterize the shell and utilize it in the production of biodiesel from algae oil.

EXPERIMENTAL

Materials and methods

Catalyst preparation

The clam shell was cleaned to remove protein and other interference substances and washed thoroughly with warm water several times. Then it was dried in oven at 105^{o}C, overnight. Crushed and powdered shell was then sieved (< 1 mm) before being subjected to heat treatment in a furnace.

Collection of algae

The algal sample in this present investigation was collected from the coastal area near Chennai, India. Algal biomass was preserved in a rectangular plastic container in open sunlight for a maximum period of 5 days. The container had dimensions of 80 cm length x 50 cm width with a liquid depth of 50 cm. During the algal storage period, the content was mixed for 15 min at a regular interval of once in every 2 h. The air supply was supplied at a rate of 1.5 m^3/h, during the photoperiod by a diffused aeration system.

Analytical methods

The total lipids were determined by extracting the algae with chloroform/methanol (2/1, v/v) and was quantified gravimetrically as percent lipid (on a dry weight basis). The potential of algal biodiesel as an alternate for diesel fuel was investigated with respect to density, ash, cloud point, flash point, pour point, cetane number, gross calorific value, water content and copper strip corrosion, based on ASTM procedures.

Extraction of algae oil

The crude extract obtained from the expression process was a mixture of lipids, water and traces of algal biomass. The extraction of lipids from the algal liquid was performed using hexane as a solvent in the separating funnel. During the extraction process the triglycerides enter into solvent layer, which was decanted and preserved for further processing. The triglyceride that was present in the hexane layer was more viscous. The residual algal biomass was subjected to further extraction of triglycerides with the addition

of hexane. The aforementioned process was conducted 3-4 times, to achieve a higher yield of extractable liquids from the expressed algae liquid.

Transesterification of algae oil

The algal lipid obtained after hexane evaporation was used in the heterogeneous transesterification without further treatment. Transesterification was carried out under varying reaction conditions. Temperature, Methanol to oil ratio and catalyst loading rate were varied in the range of 40-70^{o}C, 3 : 1 to 12 : 1 and 0.5-2% (Wt.), respectively. Acid value of oil was determined by KOH titration method.

RESULTS AND DISCUSSION

Extraction of oil from algae biomass

Hexane was used as a solvent for the extraction of triglycerides from the crude liquid extract of algal biomass. To attain a higher yield of triglycerides, the hexane was added in excess (as high as 2.5 times of that of the crude extract, on a volume basis). At a hexane to crude algal oil ratio of less than 1 : 1.5, more of the crude lipid oil was determined to be sticking on the container, thereby leading to lower yield. Hence, the volume of crude algal extract to that of hexane was maintained at a ratio of 1 : 2.5.

Transesterification

The objective of the reaction is to complete the transesterification reaction process, thereby resulting in biodiesel that was low in triglyceride concentration. In the transesterification process, an excess of methanol and nano CaO catalyst was used to ensure maximum transesterification. The completeness of reaction was ascertained by drawing the samples at different time intervals and measuring the acid value. Following the transesterification process, the biodiesel was washed with water, to remove the glycerol from the fuel.

Effect of temperature

Effect of process temperature on transesterification of algae oil was studied in the temperature range of 40 to 70^{o}C and the results are shown in Fig. 1. From the figure, it is evident that the transesterification process was facilitated by increasing the temperature up to 60^{o}C. Further increase in the temperature has not resulted in a good conversion of oil to biodiesel. It is due to the boiling point of methanol which is around 70^{o}C.

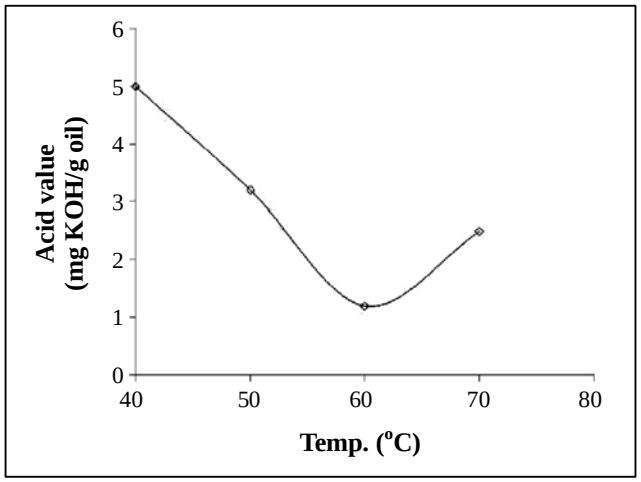

Fig. 1: Effect of Temperature on transesterification of algae oil

Effect of methanol to oil ratio

Various methanol to oil ratios were taken in the transesterification reaction of algae oil and the results are shown in Fig. 2. Transesterification is the formation of methyl esters of fatty acids present in the algae oil. Methanol is the excess reactant in this reaction, and hence added in excess quantities. In all the ratios tested in this study, 9 : 1 is considered as optimum, since the acid value of biodiesel derived by the reaction with this ratio is lowest of all. It is clearly noted from the Figure, that the acid value was high for lower methanol oil ratios. However, for the ratio of 12 : 1, the result was similar to that of 9 : 1. So 9 : 1 can be considered as an optimum value for good conversion.

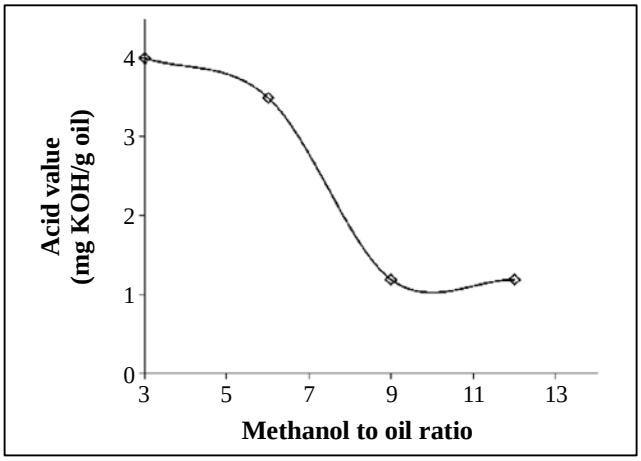

Fig. 2: Effect of methanol to oil ratio on transesterification of algae oil

Effect of catalyst loading

Effect of catalyst loading on transesterification of algae oil was studied at different catalyst loadings and the results obtained are shown in Fig. 3. When the amount of catalyst added was increased from 0.5 to 1.5% by weight, the transesterification was facilitated. Also, when the catalyst loading was increased to 2%, the transesterification was still the same as the previous value.

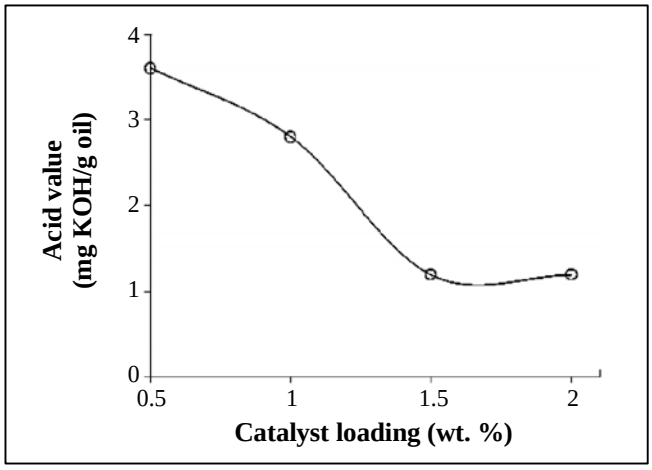

Fig. 3: Effect of catalyst loading on transesterification of algae oil

Catalyst provided necessary surface for the reaction to take place. Increasing the catalyst loading in turn increases the surface area available for the reaction. But, the reaction is limited to the level of reactant available. Therefore, further increase in the catalyst loading may not contribute to the improvement of reaction rate.

Biodiesel yield

To determine biodiesel yield per gram of dry algae biomass, about 1 gm of dry biomass was analyzed. Total Fatty Acid (TFA) content was found to be 58.2% of dry biomass i.e., 0.582 g of TFA was obtained. Under transesterfication, conversion of oil to biodiesel was about 96.3%.on the hole about 55.2% of dry biomass was converted to biodiesel, which shows the potential application of algae for the production of Alternate fuels.

CONCLUSIONS

The following conclusions were made from the present study:

(i) Algae oil is a promising source for biodiesel production.

(ii) Optimum oil yield can be obtained by using hexane as a solvent for extracting the dried algae biomass and the ratio of volume of hexane to crude oil extract was 2.5 : 1.

(iii) Optimum conditions obtained for transesterification reaction are, temperature – 60^{o}C; methanol to oil ratio – 9 : 1; catalyst loading – 1.5% (wt.).

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