

Catalytic Production of Bio-Diesel from Algal Oil

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Bio-diesel derived from oils and fats by transesterification with alcohols is a renewable, biodegradable and non-toxic fuel for compression ignition engine. As an alternate fuel bio-diesel has attracted considerable attention during the past decades. Commercial production of bio-diesel from vegetable oils is not economically viable and use of unconventional microbial sources particularly micro-algae for the production of bio-diesel is of practical significance. The present work describes conversion of algal oil to bio-diesel by transesterification with methanol in the presence of metal ion catalysts. The bio-diesel obtained was analyzed for methyl ester components and fuel related physical properties as per ASTM methods.

Key Words: Biodiesel, Algal oil, Transesterification.

INTRODUCTION

Biodiesel defined as an alkyl ester of a fatty acid is biodegradable and non-toxic fuel and is obtained from oils and fats mainly by transesterification with alcohol. It is an important alternate fuel for petroleum based diesel fuel as world's oil supplies are finite. The consumption of conventional fuels also has negative impact on environment in terms of global warming and acid rain. Biodiesel addresses these issues and can be supplemented or replace petroleum based fuels. Currently, refined vegetable oils are a major feed stock must undergo some form of pretreatment before they can be used for biodiesel production¹. The cost of raw feedstock and high processing costs limit its utility on commercial scale. While unicellular algae with simple structure represents a significant source of energy². In tons of oil produced per unit of land area algae have distinct advantage over the best oil producing crops. Production of biodiesel from algae would be cost effective and represent an attractive alternative to conventional fuels³. Transesterification has been effected by both acid, alkaline catalysts under homogeneous or heterogeneous catalytic process. Among different methods reported for biodiesel production from triglycerides, transesterification with alcohol in the presence of catalyst is commonly preferred^{4,5}. The selection of catalyst depends upon the FFA content of oil. Generally alkali catalyzed transesterification yields better conversion in short period of time but suffer from undesirable

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soap formation during the process. The present paper describes facile conversion of algal oil to biodiesel in the presence of catalytic amount of metal ions such as platinum, rhodium and ruthenium.

EXPERIMENTAL

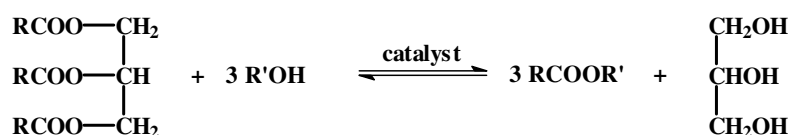
Mixed cultures of algae were collected from inlet and outlet streams of Himayat Sagar and Osman Sagar lakes situated at the out skirts of Hyderabad, India. Fermentative protocols were established to grow this mixed culture algae in the laboratory^{6,7}. The mixed cultures of algae were identified to consist of *spirogyra*, *cladophora*, *Dunaliella bioculata oscillatoria*, *paraphyridium Cruentum*. The following culture medium developed was found to be suitable for growing the mixed culture of algae. The culture media consisted 3 L of medium at 27 °C in a 5 L fermenter with composition: NaCl, 58.50 g; MgCl₂.2H₂O, 1.50 g; KNO₃, 1.0 g; MgSO₄.7H₂O, 0.5 g; KCl, 0.20 g; CaCl₂.2H₂O, 0.20 g; NaHCO₃, 0.043 mg; KH₂PO₄, 0.041 mg; K₂HPO₄, 0.50 g; FeCl₃, 0.30 g, EDTA.2Na, 5.80 g. The metal solutions consisted of the following per liter H₃BO₄, 0.61 g; MnCl₂.4H₂O, 0.23 mg; ZnSO₄.7H₂O, 0.087 mg; CuSO₄.5H₂O, 0.06 g; (NH₄)₂MO₇O₂₄.4H₂O, 0.021 mg; CoCl₂.5H₂O, 0.015mg. Mixed cultures of 1.0 kg weight was taken and cold pressed to obtain oil. The residual oil was extracted with hexane and concentrated. The combined algal oil extract was subjected to transesterification reaction.

Methanol and sodium hydroxide were of analytical grade reagents obtained from S.D. Fine chemicals. Ruthenium trichloride, rhodium trichloride and palladium trichloride were of Jhonson Mathey make. Samples of ruthenium, rhodium and palladium were prepared in methanol and estimated by literature procedures⁸⁻¹⁰. Transesterification reaction were performed in a 5.0 L three necked flask equipped with reflux condenser, thermometer and sample collection point. The reactor was immersed in a constant temperature water bath equipped with a temperature controller, that was capable of maintaining the temperature bath ± 0.2 °C. Agitation was provided with a magnetic stirrer which was set at a constant speed throughout the experiment. At the starting the reactor was filled with 1000 mL of oil obtained from algae biomass methanol (5 equivalents) and heated to 40 °C. Transesterification reactions were attempted in the presence of methanolic solutions of ruthenium trichloride, rhodium trichloride, palladium trichloride and sodium hydroxide. In all the reactions attempted a drop of catalyst in methanol (1.0×10^{-6} mol dm⁻³) was added and maintained uniformly for comparison purpose. After completion of the reaction, the reaction mixture was transferred to a beaker and was allowed to settle overnight. Of the two layers separated, the lower layer was identified as glycerol by physical and chromatographic separation tests. Of the two layers were separated, upper layer was identified as biodiesel. The upper biodiesel was cleaned through washing with water (3 times) to remove excess methanol and catalyst. Further purification was effected by heating biodiesel to 65 °C to remove methanol and moisture. The composition of methyl esters was analyzed by gas chromatography using HP

6890 series gas chromatograph system equipped with a split/splitless injection system, a flame-ionization detector and an HP chem station software (Hewlett-Packard). The column was a 30 m × 25 mm, 0.25 mm DB-wax capillary column (J.W. scientific Folson CA) with He at 25 cm/s as the carrier gas and a split ratio of 50:1 injector and detector temperatures were 250 °C. Oven temperature started at 120 °C for 2 min increased to 230 °C at a rate of 5 °C/min and held at this temperature for 5 min, methyl heptanoate was used as the internal standard.

RESULTS AND DISCUSSION

Biodiesel production involves transesterification between triglycerides and alcohol in the presence of a catalyst to produce monoesters. Complete conversion of biodiesel involves three consecutive steps with monoglyceride and diglyceride intermediates (**Scheme-I**).



Scheme-I

Among the possible alcohols, methanol is normally favoured due to its low cost. The net reaction produces 3 mol of alkyl esters and 1 mol of glycerol for each mol of triglyceride transformed. The transesterification reaction requires a catalyst in order to obtain reasonable conversion rates. Excess alcohol is used to effect higher conversion and to assist phase separation from the glycerol formed¹¹.

Mixed culture of algae was cold pressed to obtain algal oil and the residual oil was extracted with hexane. The oil was subjected to transesterification with methanol (5 equivalents) at 40 °C in the presence of a drop of methanolic solution of rhodium, ruthenium, palladium trichloride prepared in the concentration of 1.0×10^{-6} mol dm⁻³ (Table-1). The transesterification proceeds faster and in high yield compared to conventional sodium hydroxide catalyzed process. Methanolic solution of rhodium afford higher conversion compared to ruthenium and palladium under identical conditions. It is worth mentioning that the metal ion catalysts effect higher biodiesel production compared to conventional alkali catalyzed process. Though the catalyst is expensive its use in nano concentration makes it economically viable and recovery from aqueous layer was not considered.

The composition of methyl esters of fatty acids was analyzed by gas chromatography and the results are summarized in Table-2. Methyl linoleate and stearate were found to be major components. Once again rhodium catalyzed process yield biodiesel with higher percentage of esters compared to ruthenium, palladium and alkali catalyzed process.

TABLE-1
YIELD OF BIODIESEL OBTAINED IN THE TRANSESTERIFICATION REACTION
OF MIXED CULTURE ALGAL OIL

Yield of biodiesel obtained in the presence of (Yield/1000 mL of algal oil)			
Methanolic Rh ³⁺	Methanolic Ru ³⁺	Methanolic Pd ³⁺	Methanolic (NaOH)
655 mL	554 mL	498 mL	397 mL

TABLE-2
FATTY ACID METHYL ESTERS IN THE BIODIESEL DERIVED FROM ALGAL OIL
(EXPRESSED AS CONCENTRATION IN WEIGHT %)

Methyl ester	Relative content in (%)			
	Rh ³⁺ catalyzed reaction	Ru ³⁺ catalyzed reaction	Pd ³⁺ catalyzed reaction	NaOMe catalyzed reaction
Methyl linoleate	12.5	9.61	9.40	9.20
Methyl linolenate	2.10	0.18	0.15	0.14
Methyl archidate	0.60	0.40	0.38	0.36
Methyl stearate	6.50	4.40	4.00	4.00
Methyl oleate	39.0	38.5	38.2	38.2

The biodiesel was tested for fuel related properties and compared with ASTM standard values (Table-3). Flash point, viscosity, density, cloud point and cetane index comply with the limits established by ASTM relates to biodiesel quality^{12,13}.

TABLE-3
FUEL RELATED PROPERTIES OF ALGAL BIODIESEL

Fuel properties	Ru ³⁺ catalyzed	Rh ³⁺ catalyzed	Pd ³⁺ catalyzed	NaOH catalyzed	ASTM biodiesel standard
Flash point (°C) ASTM D93 A	174	171	175	170	min 100
Kinematic viscosity ASTM D445 in mm ² /s at 40 °C	4.22	4.00	4.11	4.00	3.5-5.0
Density ASTM D2709 Kg/m ³ at 15 °C	8.10	8.00	7.00	7.00	0.86-0.90
Sulphur content ASTM D2622 in ppm	1000	800	850	900	100
Cloud point (°C) ASTM D2500	4	4	3	4	-3-12
Cetane index ASTM D9737	47	45	45	40	max 49

In conclusion, transesterification of algal oil with methanol to produce biodiesel has been successfully carried out using metal catalysts. The process offers advantages in terms of mild conditions, high conversion and practical viability and may find commercial application.

ACKNOWLEDGEMENT

One of the authors, YRR thanks University Grant Commission, India for financial assistance under the Minor Research Project.

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(Received: 14 January 2009; Accepted: 16 October 2009) AJC-7962

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