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Algal biomass energy carriers as fuels: An alternative green source

Sundaram Arvindnarayan [a], Kandasamy K. Sivagnana Prabhu [b,*], Sutha Shobana [c], Jeyaprakash Dharmaraja [d], A. Pasupathy [e]

[a] Department of Mechanical Engineering, Rohini College of Engineering & Technology, Anjugramam, Kanyakumari 629 851, Tamil Nadu, India
[b] Department of Mechanical Engineering, R.M.K. Engineering College, R.S.M. Nagar, Kavaraipettai 601 206, Tiruvallur District, Tamil Nadu, India
[c] Department of Chemistry and Research Centre, Aditanar College of Arts and Science, Virapandianpatnam, Tiruchendur 628 216, Thoothukudi District, Tamil Nadu, India
[d] Department of Chemistry, Faculty of Science and Humanities, Sree Sowdambika College of Engineering, Chettikurichi, Aruppukottai 626 134, Tamil Nadu, India
[e] Department of Mechanical Engineering, Varuvan Vadivelan Institute of Technology, Krishnagiri, Gundalapattay, Dharmapuri 636 703, Tamil Nadu, India

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ABSTRACT

In this study, biomass and lipid productivity of an alga namely *Botryococcus braunii* at dissimilar nitrogen cultural environment was observed. In addition, the transesterification of algal feed stock with absolute ethanol medium in the presence of Ni catalyst with hydrogen environment and Ni(II)-Schiff base chelate as promoter was carried out to yield more algal oil as the catalyst along with promoter possesses high specific surface area, strong base strength and high base site concentration. The synthesized Schiff base and its Ni(II)-Schiff base chelate were characterized by micro elemental, spectral, thermal and XRD/SEM analyses. The quality of the extracted algal oil was analyzed using ultimate, analytical and spectral studies. In engine performance test, the algal oil–diesel blends showed a slight increase in specific fuel consumption with lower brake power. The green gas emissions were reduced for all the tested blends except $(NO)_x$. Moreover, *in vitro* antimicrobial and antioxidant activities of the algal oil extracted from the alga of dissimilar nitrogen cultural environment were studied and the results obtained show remarkable activity.

1. Introduction

Global air-pollution is a serious problem and the use of vehicles all over the world especially in big cities and towns contribute gaseous emissions, hence cause the pollution of environment. These gases referred to as green house gases (GHG) that cause global warming. GHG such as carbon dioxide (CO_2), carbon monoxide (CO), nitrogen oxides (NO_x) and sulphur oxides (SO_x) cause environmental pollution [26]. Bio-diesel is derived from vegetable oils/animal fats in the presence of suitable non polar solvent and a catalyst will be harmful to the diesel engines [12]. It may be due to their low oxidation stability & volatility, higher viscosity & density, poor fuel atomization and higher green house gases emission [29]. As our energy demand is increasing rapidly, aquatic biomass is one of the renewable energy sources to produce bio-oil which is biodegradable and improving lubricity of diesel and there is a considerable reduction of green house gases while applying algal oil in a conventional diesel engine [1]. Algal oil is an alternative to diesel fuel which has recently attracted huge attention worldwide for its good exhaust emission, sustainability and biodegradability [24]. The lipids of algal biomass can be converted into superior biofuels [16,36]. Moreover, an alga is considered as a future feedstock for biorefinery and having the ability to capture CO_2, thus creates an eco friendly environment [33]. Algal oil is formed during two step transesterification of algal feedstock which shows higher fatty acid methyl esters yield than single/direct stage process transesterification process [38,18,5] and this reaction along with quality of the yield depend upon the presence of saturated or monounsaturated fatty acids [21]. The majority unsaturated fatty acids produced by algae are linoleic acid, oleic acid, linolenic acid and palmitoleic acid [11]. The productivity of the algal feedstock surpasses the yield of the best seed crop oil [40].

* Corresponding author. Tel.: +91 9788833333; fax: +91 443330 3334.
E-mail address: kksprmk@gmail.com (K.K. Sivagnana Prabhu).

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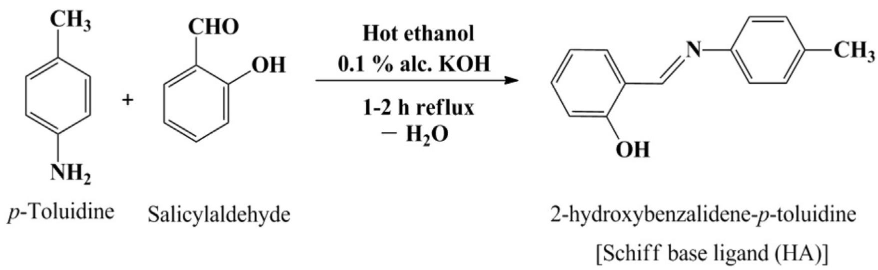


Scheme 1. Synthetic route of Schiff base ligand.

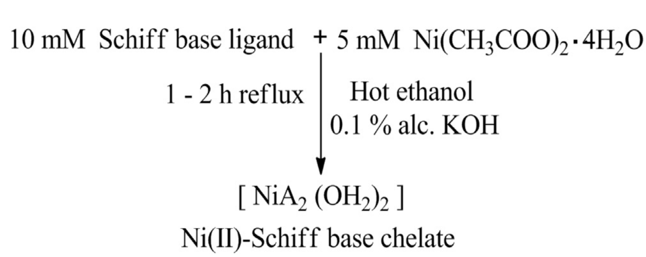
Schiff bases derived from an amine and an aldehyde containing hetero hard and soft donor atoms N, O and/or S with transition metal(II) ions have received a number of prospective technological applications, because of the high π-electron density on donor atoms in the organic moiety [13]. An attractive application of Schiff base chelates is that they not only act as promoters in the production of bio-oil from biomass feed stocks much more rapidly than acidic and basic catalysis but also prevent the bio-oil reactor vessel from the corrosion [22,43]. The Schiff base-metal promoters, with morphological features smaller than a micron at least in one dimension, have very high ratio of surface area to volume compared to the other promoters with larger grain size [27]. The transition metals included into the essential biochemical pathways are Ni(II), Cu(II) and Zn(II) ions. They tremendously enhance the activity of Schiff base due to the presence of unfilled d-orbitals which have an ability to accept electrons. The significance of Ni(II) catalyst is due to its redox chemistry, high natural profusion and low price in the hydrotreatment of algal feed stock [45]. The Schiff base chelates are more popular and most preferred in the commercial production of algal oil due to their low cost and availability. Algal oil–diesel blends are widely used as power sources in medium and heavy-duty applications because of their low emission of carbon monoxide (CO) and hydrocarbons (HC) compared to gasoline engines [44].

In this work, the biomass and lipid productivity at dissimilar nitrogen cultural environment the alga namely *Botryococcus braunii* was observed. For the first time, a two step transesterification reaction of algal feed stock from an alga namely *B. braunii* in the presence of Ni catalyst with hydrogen environment and Ni(II)-Schiff base chelate as promoter in absolute alcohol medium was carried out. The structure of Ni(II)-Schiff base chelate has been confirmed by micro elemental, spectral, thermal and XRD/SEM analyses. The quality of the algal oil was analyzed using ultimate, analytical and spectral studies. Moreover, the engine performance and emission tests for the algal oil–diesel blends, *in vitro* microbial and antioxidant activities of the algal oil were studied.

2. Experimental

2.1. Materials and methods

All the chemical products and solvents were purchased from E. Merck, Sigma Aldrich and S.D. Fine chemicals. *B. braunii* were collected and isolated from Kovalam solar salt works in Kanyakumari of India. 2,2-diphenyl-1-picrylhydrazyl (DPPH) and ascorbic acid (AA) were purchased from Sigma Aldrich. Schiff base (2-hydroxybenzalidene-*p*-toluidine) and Ni(II)-Schiff base chelate were synthesized in our laboratory. Solvents used in the physical measurements were of analytical grade and were purified according to the literature [32]. Melting point of Schiff base and its metal chelate was determined on Gallenkamp apparatus in open glass capillaries and was uncorrected. Metal content of the chelate was estimated gravimetrically by standard procedures [42]. Molar conductance of the chelate was measured in DMSO solvent using Elico CM 180 Conductivity Bridge using 0.01 M KCl solution as calibrant. The micro elemental and ultimate analyses of C, H, N and S were performed on Elementar Vario EL III CHNS analyzer at STIC, CUSAT, India. Temperature was adjusted to 25 ± 2 °C. Infrared spectra were recorded using KBr pellets on a JASCO FT/IR-410 spectrophotometer in the 4000–400 cm^{-1} range. Fast atomic bombardment mass spectra (FAB-MS) were recorded using a VGZAB-HS spectrometer in a 3-nitrobenzylalcohol matrix. Magnetic susceptibility measurements were carried out on a Gouy balance at room temperature using mercuric tetra(thiocyanato)cobaltate(II) as the calibrant. Diamagnetic corrections were applied in compliance with Pascal's constant [14]. Electronic absorption spectra were recorded with a Hitachi U-2000 double beam spectrophotometer in the 200–1100 nm range. Fatty acid compositions of algal oil were determined using gas chromatography techniques (GC) and were performed on Shimadzu gas chromatograph equipped with flame ionization detector and capillary column (30 m × 0.25 mm × 0.25 μm film). The detector temperature was programmed for 280 °C with the flow rate of 0.3 mL/min and the injector temperature was set at 250 °C. Nitrogen gas was used as the carrier. ^{1}H NMR and ^{13}C NMR spectra of the algal oil were carried out in DMSO-d_6 at room temperature using TMS as internal standard on a Perkin Elmer R-32 spectrometer.



Scheme 2. Synthetic route of Ni(II) Schiff base chelate.

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