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Biodiesel synthesis from microalgal lipids using tungstated zirconia as a heterogeneous acid catalyst and its comparison with homogeneous acid and enzyme catalysts

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HIGHLIGHTS

- Tungstated zirconia used for conversion of *S. obliquus* lipids.
- Tungstated zirconia showed 94.58% FAME conversion and reuse up to 3 batches.
- Heterogeneous catalyst showed comparable conversion with homogeneous catalyst.
- Heterogeneous catalyst showed higher conversion than enzyme catalyst.
- Time requirement for tungstated zirconia catalysis was lowest.

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ABSTRACT

Downstream step of catalytic conversion is scarcely investigated area in microalgal biodiesel production process. In this study a heterogeneous acid catalyst, tungstated zirconia (WO_3/ZrO_2) is evaluated for conversion of *S. obliquus* lipids. Catalytic efficiency of tungstated zirconia catalyst was compared to the homogeneous acid catalyst and enzyme catalyst in terms of conversion efficiency, reaction parameters, energy consumption and reusability. Tungstated zirconia catalyst showed maximum biodiesel conversion of 94.58% at 100 °C temperature, 12:1 methanol to oil molar ratio and 15% of catalyst amount based on oil weight in 3 h. Tungstated zirconia showed comparable biodiesel conversion to homogeneous catalyst and higher conversion than the enzyme catalyst. The time requirement for heterogeneous catalyst was lowest, while, the energy consumption was highest among the selected catalysts. Most of the fuel properties of biodiesel synthesized by tungstated zirconia catalyzed conversion of *S. obliquus* lipids comply with the specifications set by ASTM and EN standards.

1. Introduction

Biodiesel is considered as renewable alternative for fossil fuel. With the increase in fossil fuel prices and environmental concerns, biodiesel production is expected to grow higher [1,2]. Microalgae has shown promising potential as a sustainable biodiesel feedstock [3,4]. Transesterification of lipids to biodiesel in presence of methanol and suitable catalyst is the widely accepted route for biodiesel production. Industrial scale biodiesel production plants are currently applying the conventional homogeneous chemical catalyst for conversion of feedstock lipids [5]. The conventional homogeneous catalyst even though offer high yields, but are associated with several drawbacks such as extra neutralization step, tedious purification process and wastewater generation [6]. The treatment of wastewater also adds to the production cost of the biodiesel.

Heterogeneous catalysts are gaining interest for conversion of oils to biodiesel due to its advantage of easy separation from reaction mixture and reuse [7]. The heterogeneous catalyst has shown potential to overcome the challenges of homogeneous catalyst and replacing it at industrial scale. The downstream processing of microalgal lipids for biodiesel synthesis more specifically its catalytic conversion is not intensively studied area. The commercial realization of microalgal biodiesel is still challenging due to its high production cost. The reuse potential of heterogeneous catalyst and minimal wastewater generation can improve the microalgal biodiesel production economics. The other challenge with microalgal lipids is its high free fatty acid content which poses difficulties in

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conversion process [8]. The conventional alkali catalyst leads to the soap formation in presence of high free fatty acid which hampers the biodiesel yield [9]. Thus it is suggested to use either the two step process or acid catalyst for conversion of feedstock oils with high lipid content [10]. Tungstated zirconium oxide (WO_3/ZrO_2) is a heterogeneous solid acid catalyst which has been successfully utilized for biodiesel production from vegetable oils [11], however; it has not been studied for microalgal lipids conversion. Also to the best of our knowledge none of the previous study reports the comparative evaluation of various types of catalysts for conversion of microalgal lipids. In this study we have investigated the tungstated zirconia catalyzed conversion of *S. obliquus* lipids. Response surface methodology (RSM) was used to optimize the reaction parameters. We have also studied the efficiency of this heterogeneous acid catalyst as compared to conventional homogeneous acid catalyst and enzyme catalyst in terms of conversion, reaction parameters and energy input.

2. Materials and methods

2.1. Chemicals and reagents

Ammonia solution (25%) (AR) was procured from Associated Chemical Enterprises (ACE), South Africa. Zirconyl chloride octahydrate was obtained from Sigma-Aldrich and ammonium metatungstate hydrate was obtained from Fluka Analytical, Germany. The *Pseudomonas fluorescens* lipases immobilized on immobead 150 (Sigma-Aldrich, Netherlands) was obtained from Sigma-Aldrich. A mixed fatty acid methyl ester (FAME) standard (37 components) and methyl heptadeconoate were obtained from Sigma-Aldrich, USA. All organic solvents and other chemicals were of analytical grade.

2.2. Cultivation of microalgae and lipid extraction

S. obliquus was grown in open raceway pond (3000 L) on modified BG11 nutrient medium with limited nitrogen (750 mg L^{-1}) and iron supplementation (9 mg L^{-1}) for ensuring high lipid accumulation [12]. The cultivation conditions were water temperature 20–25 °C, natural light condition (600–1200 μmol m^{-2} s^{-1}), mixing and aeration was accomplished by two submersible pumps with flow rate of 110 L min^{-1}. The biomass yield of *S. obliquus* was monitored by gravimetric analysis. Dewatering is required to obtain thick biomass slurry. Harvesting of biomass was initially done on day 14 by gravitational settling to remove the bulk amount of water followed by centrifugation to obtain thick slurry. All the biomass required for study was collected from same batch of open pond cultivation. Biomass was then freeze dried using lyophilizer. Lipids were extracted from freeze dried biomass using microwave assisted solvent extraction. Solvents used were chloroform and ethanol in 1:1 (v/v) ratio [13]. Saponification and acid value of extracted lipids was determined by ASTM methods D5558-95, reapproved 2011 and D664-07 respectively [8]. Lipids extracted from *S. obliquus* were used for catalytic conversion study.

2.3. Catalyst preparation and characterization

The heterogeneous acid catalyst, tungstated zirconia (WO_3/ZrO_2) was prepared and characterized by the method described in our previous publication [14]. Firstly $Zr(OH)_4$ was synthesized by precipitation of zirconium oxychloride hydrate ($ZrOCl_2{\cdot}8H_2O$) with ammonia solution (25%) at pH around 8.0–8.5. Then $Zr(OH)_4$ was thoroughly washed with water to remove chloride salts followed by drying at 100 °C for 24 h. The dried $Zr(OH)_4$ was ground to powder in mortar. $Zr(OH)_4$ was then impregnated with ammonium metatungstate hydrate [$(NH_4)_6(H_2W_{12}O_{40})$ nH_2O] (50 wt%). The impregnated powder was calcined at 800 °C for 4 h to produce tungstated zirconia. FTIR analysis of the catalyst was carried out using FTIR spectrophotometer (Spectrum Bx FTIR System, Perkin Elmer). FTIR spectra were obtained between 4000 and 400 cm^{-1} on KBr powder. The FT-IR spectrum of pyridine adsorbed catalyst was carried out to on an ATR spectrometer at room temperature to find the nature of acidity of Brønsted and Lewis acid sites. Pyridine adsorption was carried out by placing a drop of pyridine on few mg of the catalysts followed by evacuation in air for 1 h at room temperature to remove the reversibly adsorbed pyridine. Catalyst was also characterized for phase analysis by XRD. Thermogravimetric analysis was done to analyze thermal behaviour and degradation of the prepared catalyst. TGA-DSC analysis was performed using TA instrument (SDT Q600). The programmed range for heating was from room temperature to 800 °C at the rate of 10 °C min^{-1} under a nitrogen atmosphere.

2.4. Catalytic conversion of microalgal lipids

The tungstated zirconia as a heterogeneous catalyst, sulphuric acid as a homogeneous chemical catalyst and immobilized *Pseudomonas fluorescence* lipase as an enzyme catalyst were used for conversion of microalgal lipids to biodiesel.

The reaction conditions for heterogeneous acid catalyzed conversion were optimized using a three level three factorial Box-Behnken response surface methodology (RSM) experimental design using Minitab statistical software. The temperature, catalyst concentration and methanol to oil molar ratio were taken as the factors. The three levels for the selected factors were determined by the preliminary experiments and previous literature and depicted in Table 1. Microalgal oil conversion (FAME) was taken as the response to determine the optimized parameters. The reaction time was determined by preliminary experiment at 50 °C, catalyst amount 5% w/w of oil, methanol to oil molar ratio of 9:1, hexane 1 ml. The optimized time, 1 ml hexane as reaction solvent and agitation speed of 200 rpm were kept constant for all other reactions. All the reactions were carried out taking 0.1 g of microalgal lipids as feedstock.

The effect of independent factors on the dependent factors was analyzed by a quadratic equation:

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_{11}X_1^2 + a_{22}X_2^2 + a_{33}X_3^2 + a_{12}X_1X_2 + a_{13}X_1X_3 + a_{23}X_2X_3 + e \quad (1)$$

where Y is the response (biodiesel conversion, %), a0 is offset term; a_1, a_2 and a_3 are linear coefficients; a_{11}, a_{22} and a_{33} are the squared term coefficients; a_{12}, a_{13} and a_{23} are the interaction coefficients; and e is the error. X_1, X_2 and X_3 are temperature, methanol to oil molar ratio and catalyst amount respectively.

The reaction conditions for homogeneous acid catalyst were, methanol to oil molar ratio of 30:1; temperature: 60 °C; catalyst concentration: 10% w/w of oil; time: 4 h; hexane: 1 mL [15]. The reaction conditions for enzyme catalyzed conversion were temperature: 35 °C; catalyst concentration: 10% w/w of oil; water content: 2.5% w/w of oil; time: 12 h; hexane: 1 mL and methanol to oil ratio of 3:1 where 1 mol methanol is added in 3 steps (0, 3 and 6 h) [16].

Table 1
Factors and levels for experimental design using tungstated zirconia catalyst.

Factors	Temperature (°C)	MeOH:oil molar ratio	Catalyst conc. (wt% with respect to oil weight)
Level 1	−1 (60)	−1 (9:1)	−1 (5)
Level 2	0 (80)	0 (12:1)	0 (10)
Level 3	1 (100)	1 (15:1)	1 (15)

MeOH-Methanol.