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Research Article

Production of biodiesel from *Catharanthus roseus* biooil using $BaMoO_4/TiO_2$ as a heterogeneous acid catalyst

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Abstract

At present, most countries in the world are the importers of energy. The major demand in the energy system occurs, especially for crude products. Biodiesel is eco-friendly and it's derived from vegetable oil, animal fat, waste cooking oil and non-edible oils. In the present study, non-edible oil from *Catharanthus roseus* seeds was utilized to produce biodiesel with the help of a heterogeneous catalyst. Barium Molybdate ($BaMoO_4$) doped with Titanium dioxide (TiO_2) used as a sole heterogeneous catalyst was prepared using ultrasonication technique at 610°C for 5 h and used for producing biodiesel. The catalyst was characterized by XRD, FT-IR, SEM, TGA and EDAX analysis.

Keywords: *Catharanthus roseus*; Oil extraction; Transesterification; Heterogeneous catalyst; Biodiesel.

Introduction

The cost of fuels is rapidly increasing due to their heavy demand and the crude fuel simultaneously release emissions causing severe health hazards, acid rains, and environmental pollution an alternative fuel is in a great logical frame, ecologically manageable, financially achievable and ready to use [1]. The alternative source for fossil fuels in earlier days was collected from animal waste, corn oil, canola oil etc and lately the bio-oil is extracted from non-edible crops. Biodiesel is obtained from a variety of sources like vegetable oil, animal fat, waste cooking oil and non-edible oil. Biodiesel is synthesized by transesterification of triglycerides which reacts with alcohol in the presence of the catalyst [2, 3]. Chemically, production of of biodiesel named as FAME (fatty acid methyl esters), this process is generally referred to as transesterification [4-6].

Biodiesel has similar properties to that of the crude diesel fuel and used for automobiles. Catalysts are used in the manufacture of fuels like gas, diesel oil, petrol oil etc [7-9]. The creation of clean vitality from sustainable power sources, such as hydrogen for energy units and transportation fuels from non-consumable biomass are catalyst dependent processes.

Catalyst forms can be established in two ways homogeneous and heterogeneous. The homogeneous catalyst used for profit-making, the disadvantage is that the corrosion occurs in the apparatus. Compared to heterogeneous catalysts, homogeneous catalyst reacts quickly and is non-destructive in nature [10]. Also the division of fluid will be simple, steady and long-standing. Many methods of the transesterification process of oil to biodiesel. Some of them are non-catalytic supercritical, conventional, microwave and ultrasound. Out of this ultrasonication technique is widely used for a variety of feedstocks [11-13]. In the present study, transesterification *Catharanthus roseus* biooil into biodiesel using $BaMoO_4/TiO_2$ as a heterogeneous acid catalyst was optimized.

Materials and methods

Materials and Extraction of oil

Catharanthus roseus seeds are found from the botanical garden and from the local areas of Thanjavur in Tamilnadu state, India. Solvents and chemicals of anhydrous grade (99.99%) such as Methanol, Barium Chloride, Titanium dioxide, Barium nitrate tetrahydrate, and molybdic acid collect from SRL Chemicals Pvt. Ltd., Mumbai in Maharashtra state, India. The extraction processes was carried out by

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using a Soxhlet apparatus and with the help of a heating coil at 65°C for 3 h [14].

Preparation of sustainable and clean catalyst

The 0.2 moles of titanium dioxide was added to 100 ml of distilled water at room temperature for 10 min under magnetic stirring. The solution was kept at 30°C overnight and the product of the white precipitate collected. The titanium dioxide nanoparticle was doped by barium salt of molybdic acid. In the present study, 10 moles of titanium dioxide support has impregnated into 20 ml of solution to 1 mole of barium nitrate tetrahydrate at constant stirring. The mixed solution evaporated at 80°C for 3 h and dried overnight at 110°C.

The resultant white precipitates calcined at 610°C for 5 h. In the second step, the calcined titanium supported barium nitrate tetrahydrate is added into a 20 ml solution containing 1 mole of molybdic acid with continuous stirring and on completion of the addition, the mixture was dried at 110°C and calcined at 610°C for 5 h, a clear white $BaMoO_4/TiO_2$ is obtained.

Transesterification reaction against bio oil

Transesterification reaction was carried out in a 500 ml glass container placed in a condenser, surrounded by a cooling jacket with the help of heating mantle and controlled by the temperature controller [15, 16]. The alcohol and *C. roseus* oil in the ratio 16:1 was heated to a temperature of 65°C by radiation of the ultrasonication method, with the addition of prepared heterogeneous catalyst. Inside the reactor, the temperature was raised to 65°C under stirring at 450 rpm the process of transesterification reaction takes place for 2 h.

Characterization of the catalysts

Physico-chemical characteristics which are responsible for its performance of $BaMoO_4/TiO_2$ as heterogeneous nanocatalyst were studied. Characteristics of the nanocatalyst include surface and morphological characteristics, crystal structure, and thermal stability were analyzed using scanning electron microscope (SEM) with Energy Dispersive X-ray Analysis (EDAX), X-ray powder diffraction (XRD) and thermal gravimetric analysis (TGA).

Results and discussions

Effect of reaction temperature on transesterification

The effect of reaction temperature on transesterification of *C. roseus* seeds oil using $BaMoO_4/TiO_2$ heterogeneous catalyst is shown in figure 1. The temperature of the reaction was maintained at 45, 55 and 65°C. The increase in temperature from 45 to 65°C resulted in an increase in the yield of methyl esters in 30 min reaction time. The optimum reaction temperature was found to as 65°C for transesterification reaction to *C. roseus* seed oil to biodiesel using alcohol to oil ratio 16:1 and a catalyst amount of 0.5 wt%.

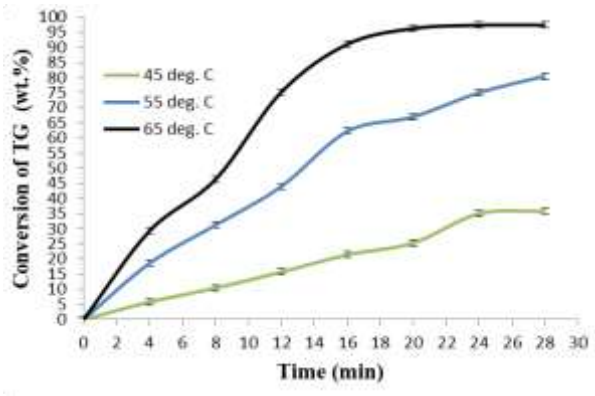

Figure 1. Effect of reaction temperature

Effect of the molar ratio of methanol to oil

One of the major variables affect the yield of esters is the molar ratio of alcohol to triglycerides. From the figure 2 it is found that the conversion of triglycerides increases for increase in molar ratio of alcohol to oil from 12:1 to 16:1 and decrease with increase in molar ratio of alcohol to oil above 16:1. The highest yield of methyl esters 98.10% is obtained from the molar ratio of alcohol to oil at 16:1. From these results, the molar ratio of 16:1 is found as the optimum methanol to oil ratio.

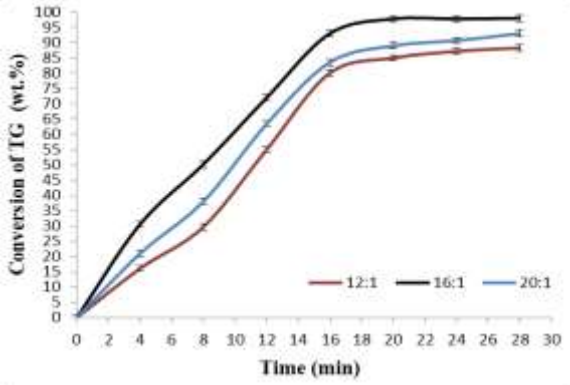

Figure 2. The effect of molar ratio of methanol to oil

Effect of mass ratio of catalyst loading

The effect of mass ratio of catalyst loading on transesterification of *C. roseus* seeds oil using $BaMoO_4$ /TiO_2 heterogeneous catalyst is shown in figure 3. The mass ratio of catalyst loading of was varied at 0.25, 0.5 and 0.75 wt% with the reaction temperature of 65°C. The optimum catalyst loading was found as 0.5% and maximum conversion of oil in to biodiesel was 98.10% at 30 min.

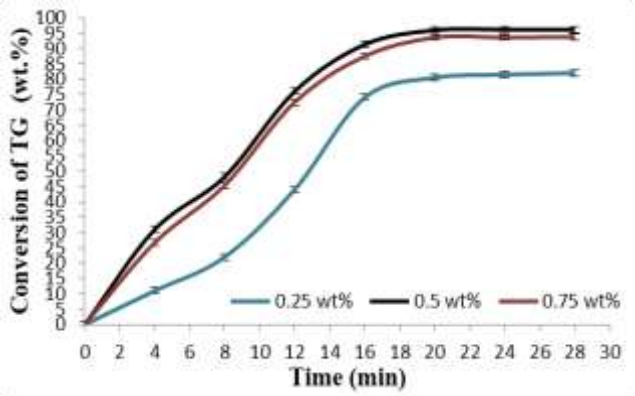

Figure 3. Effect of catalyst loading

Effect of catalyst reusability on the transesterification reaction

The main reasons for the repeated usage of catalyst in transesterification reaction are to decrease the cost of production present in biodiesel. The effect of catalyst reusability on the transesterification reaction is shown in figure 4. The $BaMoO_4$ /TiO_2 heterogeneous catalyst is highly stable and active for several cycles. The recovered catalyst charged regular runs without any pre-treatments and the results of the catalyst amount collected safely and recycled. Subsequently, $BaMoO_4$ / TiO_2 heterogeneous catalyst results in less cost of production of biodiesel because of its more drawn out lifetime catalyst and stability.

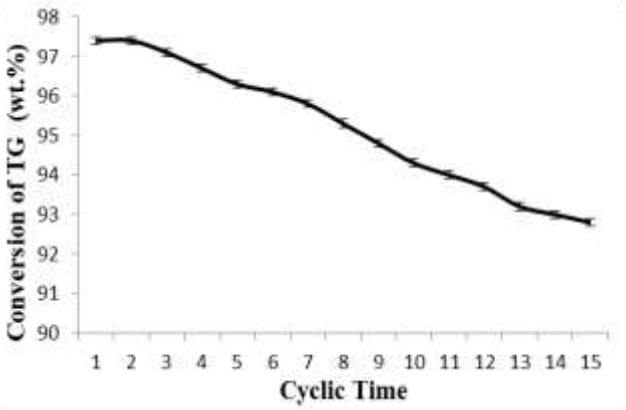

Figure 4. Catalyst reusability

Characterization of $BaMoO_4$ doped with TiO_2 nanocatalyst

Thermogravimetric and X-ray diffraction analysis

Thermogravimetric analysis (TGA) has done in a Netzsch instrument (STA 449C, Netzsch, Seligenstadt, Germany). The heating range was between 30 °C and 800 °C at a rate of 10°C/min under a nitrogen atmosphere. The measure has done for 5-10 mg of samples and the results are shown in figure 5.

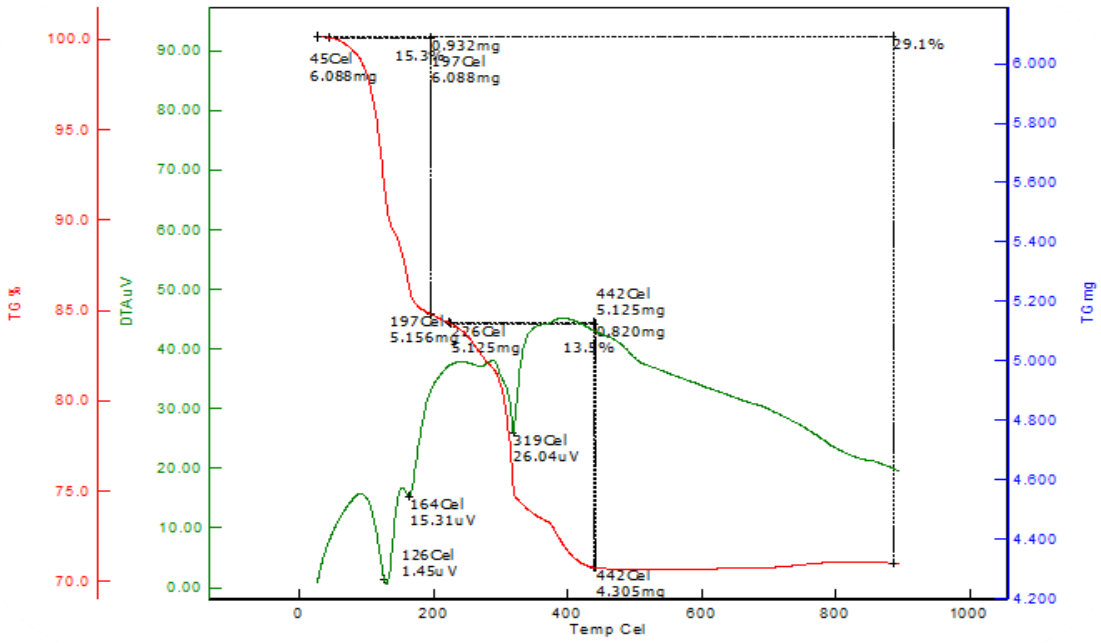

Figure 5. Thermogravimetric analysis of $BaMoO_4$ doped with TiO_2 nanocatalyst

X-ray diffraction (XRD) patterns of the samples had examined using a reflection scan with nickel-filtered Cu Ka radiation (D8, Bruker-AXS, Germany). The measurement was performed at 2 theta degrees between 10 and 80 in figure 6. The typical peaks of pure $BaMoO_4$ obtain 2θ°=17.21, 27.81, 31.82, 36.39. In this study $BaMoO_4$ doped with TiO_2 the pure magnesium and titanium compounds present in 2θ°=25.28, 36.94, 37.80, 48.05, 62.69. These results confirm the heterogeneous catalyst $BaMoO_4$ and TiO_2 as an active catalyst.

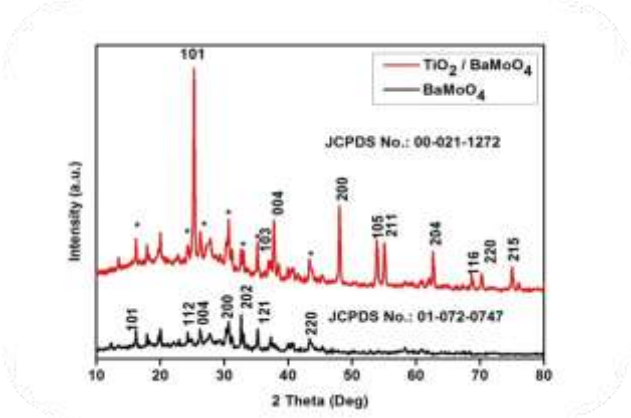

Figure 6: XRD of $BaMoO_4$ doped with TiO_2 nanocatalyst

Scanning electron microscopy and Energy Dispersive X-ray Analysis

Scanning electron microscopy (SEM) images had obtained with 20-kV accelerating voltage using a field emission scanning electron microscope (S-4800, HITACHI Corp., Tokyo, Japan). SEM images of TiO_2 and $BaMoO_4$ / TiO_2 are shown in figure 7. The SEM descriptions of $BaMoO_4$, $BaMoO_4$ / TiO_2 samples show crystallites of 1 µm size. Figure 8 shows the EDAX analysis and confirms that the presence of elements as Ti, O, Mg and Mo in the catalysts with the silica peak. The EDAX analyses show that the $BaMoO_4$ / TiO_2 catalysts have been synthesized successfully step by step with high purity. The analyzed values were almost equivalent to the predicted values (Table 1).

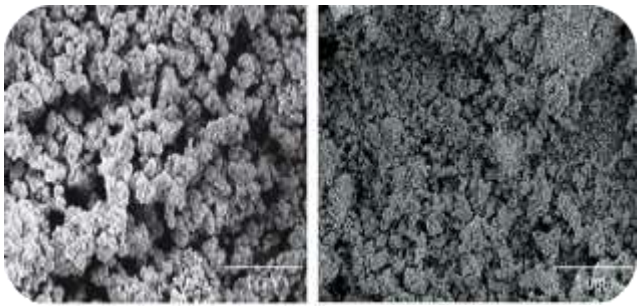

Figure 7. SEM images of $BaMoO_4$ doped with TiO_2 and TiO_2 nanoparticles

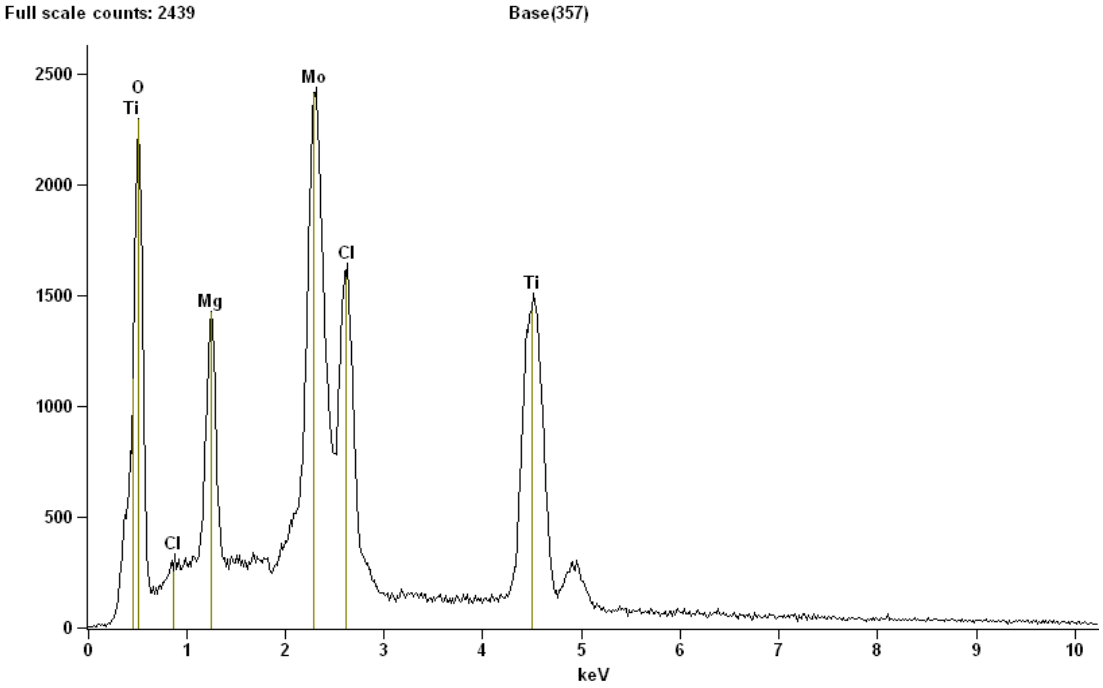

Figure 8. EDAX of $BaMoO_4$ doped with TiO_2 nanocatalyst

Characterization of Catharanthus roseus biodiesel

The *C. roseus* biooil was pre-treated by esterification process to reduce their acid value, esterification originated to be appropriate for the transesterification process. The reaction conditions were optimized to increase the conversion to biodiesel production. The best consequence of 98.10 % of methyl ester yield

was acquired from *C. roseus* oil under optimum condition of 0.5 wt % of catalyst and 16:1 molar ratio of methanol to oil at 65°C temperatures for a reaction time of 30 min. The resultant product of biodiesel was analyzed by standard ASTM methods and compared with standard ASTM D6751 values in table 2. The conversion to biodiesel was calculated by ^{1}H-NMR analysis shown in figure 9.

Table 1. Quantitative analysis of $BaMoO_4$ doped with TiO_2 nanocatalyst by EDAX

S.No.	Element	Net Counts	Weight %	Atom %
1	O	22526	38.98	66.34
2	Mg	13039	4.83	5.41
3	Cl	22696	10.35	7.95
4	Cl	0	---	---
5	Ti	27848	25.62	14.57
6	Ti	4857	---	---
7	Mo	41622	20.22	5.74
8	Mo	0	---	---
	Total		100.00	100.00

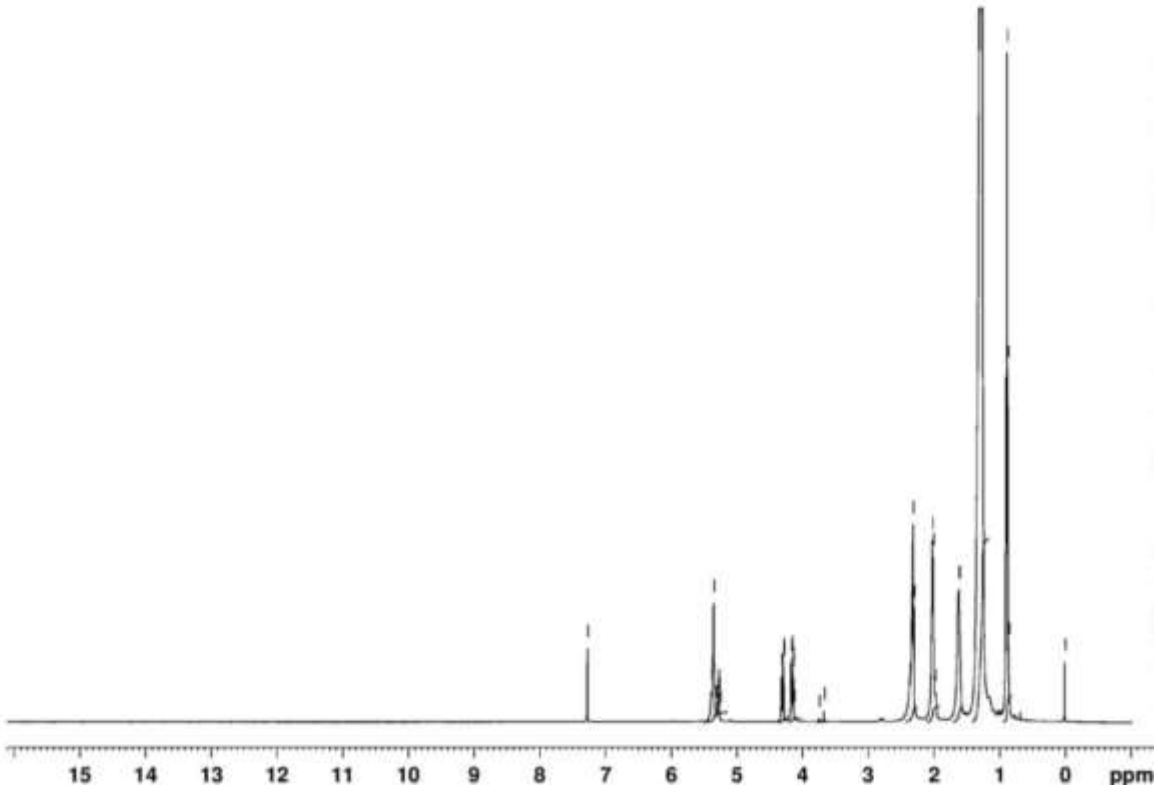

Figure 9. ^{1}H-NMR spectrum of *Catharanthus roseus* biodiesel

Table 2. Fuel characteristics of *Catharanthus roseus* biodiesel

S. No.	Properties	Units	ASTM method	ASTM limits (D6751)	*C. roseus* biodiesel
1	Specific Gravity	-	D 4052	-	0.781
2	Flash Point	° C	D 93	130 min	149
3	Cloud Point	° C	D 2500	report	2
4	Pour Point	° C	D 2500	report	-4
5	Kinematic Viscosity @ 40°C	mm^2/s	D 445	1.9 to 6.0	4.98
6	Acid Number	mg KOH/g	D 664	0.05 max	0.039
7	Cetane Number	-	D 613	47 min	49
8	Copper Strip Corrosion	-	D 130	Max number 3	1a

Conclusions

C. roseus oil into biodiesel yield was made to be higher; it is utilized as a potential source to produce biodiesel. Results shows that the TiO_2 doped with $BaMoO_4$ is an effective as heterogeneous catalyst prepared wet impregnation method followed by calcination at 610°C for 5 h. Throughout, this work transesterification reaction of *C. roseus* seeds oil

to biodiesel exceeds 98.0% with 30 min using 16:1 methyl alcohol to oil ratio at 65°C. Thus the economical and effective production biodiesel from *C. roseus* seed oil was achieved.

Conflicts of interest

The authors declare no conflict of interest.

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