CATALYTIC CONVERSION OF THEVETIA PERUVIANA OIL INTO BIODIESEL BY TiO_2-ZnO NANOCATALYST

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Abstract

Exploration of new heterogeneous catalyst for biodiesel production and the use of non-edible vegetable oils as a sustainable source favourably could contribute to bioenergy research. In this regard the present investigation aims to demonstrate the catalytic activity of TiO_2-ZnO nanocatalyst towards the biodiesel production from Thevetia Peruviana oil. The prepared catalyst has been characterized through XRD, FT-IR and SEM techniques. We have used Thevetia Peruviana oil as a non-edible vegetable oil feedstock for biodiesel production. This oil seed bearing tree species is widely available in the North-Eastern region of India. Biodiesel has been produced by transesterification process in which Thevetia Peruviana oil is allowed to react with methanol in 1:6 molar ratio, in presence of TiO_2-ZnO nanocatalyst comprising 6 wt% of the oil. The temperature was maintained at 65^0C and the reaction was allowed to run for 5 hours maintaining rpm 600. The synthesized biodiesel is then characterized using ^{1}HNMR technique. The conversion of biodiesel has also been determined using ^{1}HNMR technique and was found to be 94.11% . This study proves to be beneficial in the exploration of heterogeneous catalysts for biodiesel production because heterogeneous catalytic transesterification have many advantages over homogeneous transesterification such as catalyst can be recycled, lesser amount of waste water produced and separation of biodiesel from glycerol is easier. The use of nanocatalyst shows higher catalytic activity, easier to separate and reusable that produces improved biodiesel fuel at very low cost. The TiO_2-ZnO nanocatalyst shows good catalytic performance and hence can be used for large scale biodiesel production from Thevetia Peruviana oil

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1. INTRODUCTION

The energy demand across the world is increasing today. The major energy demand is fulfilled from fossil fuels such as coal, petroleum and natural gas. But due to the diminishing fossil reserves as well as various environmental issues renewable energyresources is becoming more and more attractive. Among various renewable energy sources, biodiesel has gained worldwide popularity due to its renewable, non-toxic, biodegradable andclean combustion properties[1,2]. Biodiesel can be produced by transesterification of vegetable oil (both edible and non-edible) or animal fat with an alcohol (usually methanol or ethanol) in presence of a suitable catalyst. When edible oils are used as a feedstock for biodiesel production food resources are actually converted to automotive fuels which may bring huge imbalance in human nutrition versus fuel. To overcome this, research work has been done to produce diesel fuel from alternative and greener resources such as non-edible oil seeds because of its low price which in turn reduces the overall cost of biodiesel production. Moreover non-edible oil seeds are readily available and doesnot compete with food supply[3]. Theconventional method of biodiesel production is through transesterification using various homogeneous base and acid catalysts such as sodium hydroxide, potassium hydroxide, sulphuric acid and p-toluene etc. But homogeneous catalysts has certain drawbacks such as they are corrosive, sensitive to free fatty acids that leads to formation of soap during the transesterification process and hence an additional treatment is required to remove the soap which involves additional processing time and overall cost [4]. Heterogeneous catalysts have great advantages over homogeneous catalystsas it requires easier catalyst operation andseparation, reuse and regenerate thus lowering the cost of production. Alkali metal oxides and derivatives [5,6], alkaline earth metal oxides and derivatives [7,8,9,10], transition metal oxides and derivatives [11,12], mixed metal oxides and derivatives[13-17], ion exchange resins type acid heterogeneous catalyst [18,19],carbon based heterogeneous catalysts[20,21], waste material based heterogeneous catalysts [22,23], enzyme based heterogeneous catalyst [24] were reported in the recent years and their uses in laboratory scale biodiesel production. But most heterogeneous catalyst has limitations such as they require high reaction time, high reaction temperature and low catalytic stability which gives low yield of product due to slow reaction rate. Nanomaterials with large surface to volume ratio and high catalytic surface can overcome the problems associated with heterogeneous catalyst such as mass transfer resistance, fast deactivation, inefficiency and time consumption by achieving ideal reaction condition [25,26]. Wide range of nanocatalysts [26,27-33]are being synthesized in the recent years and their performance was evaluated for the synthesis of biodiesel.

The present work is focussed on the synthesis of TiO_2-ZnO nanocatalyst for the efficient production of biodiesel using Thevetia Peruviana oil seeds as feedstock. The prepared catalyst was characterized through XRD, FT-IR & SEM techniques and the conversion of biodiesel has been done through ^{1}HNMR technique.

2. MATERIALS AND METHOD

2.1 Materials Used

The chemicals used for the synthesis of titanium dioxide-zinc oxide nanocatalyst and production of biodiesel were titanium(IV)n-butoxide{$Ti[O(CH_2)_3CH_3]_4$}, isopropyl alcohol{$(CH_3)_2CHOH$}, nitric acid{HNO_3}, zinc acetate dehydrate{$(CH_3COO)_2Zn.2H_2O$} and methanol{CH_3OH}.All the chemicals are of analytical grade and used without purification. Thevetia Peruviana oil was purchased from a local nursery.

2.2 Synthesis of TiO_2-ZnO Nanoctalyst

TiO_2-ZnO nanocatalyst was synthesised by sol-gel method. Initially titanium(IV)n-butoxide and isopropyl alcohol was mixed in the required proportion to get the sol. To this 1ml conc. HNO_3 and small amount of water was added dropwise under constant stirring. After that the solution of zinc acetate dehydrate-isopropyl alcohol was slowly added to it.Than it was stirred for 12 hours to get the gel.The prepared sample was then dried at 45^0C followed by calcination at 450 ^{0}C for 2 hour at ramping rate of 4^0C/min to get TiO_2-ZnO nanocatalyst.

2.3 Characterization of TiO_2-ZnO Nanocatalyst

The phase structure of the calcined nanocatalyst was studied using XRD (Rigaku Miniflex, Japan) using CuKα (λ= 1.541A^0)radiation at 30 kVin the 2Θ range of 20-70^0. The surface morphology and shape of the synthesized catalyst was analyzed using SEM (Jeol 6390LV, Japan) operated at an accelerating voltage of 20 kV. FT-IR spectra of the samples were recorded using FT-IR spectrometer (Nicolet Impact410, USA).

2.4 Transesterification of Thevetia Peruviana Oil using TiO_2-ZnO Nanocatalyst

The reaction was carried out in a 3-neck round bottom flask, which is immersed in a constant temperature water bath placed above the plate of a magnetic stirrer. The flask is fitted with a condenser in the middle neck and a thermometer in the side neck.The transesterification of Thevetia Peruviana oil was carried out by reacting oil and methanol in 1:6 ratio in presence of 6 wt% of the catalyst(with respect to oil). The reaction was allowed to run for 5 hoursmaintaining temperature at 65^0C and rpm 600 (fig.1). After completion of the reaction the solid catalyst was separated by filtration. The productobtained was heated to remove excess methanol and than allowed to settle in a separating funnel. The upper liquid phase consists of fatty acid methyl ester(biodiesel) and lower liquid phase consists of glycerol as the by product. The product obtained was characterized using ^{1}HNMR to determine the conversion of methyl ester. ^{1}HNMR spectra was recorded on Jeol JNM-ECS400 NMR spectrometer at 25.5^{0}C using CDCl3 as a solvent and Tetrametylsilane (TMS) as an internal standard respectively.

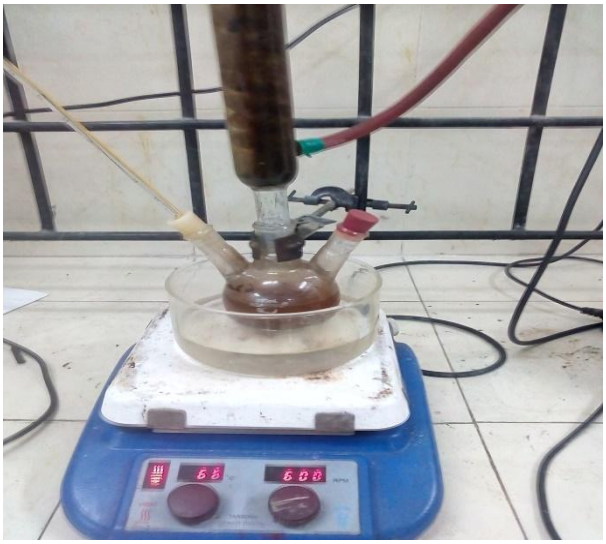

Fig.1 Experimental set up for transesterification of Thevetia Peruviana oil.

3. RESULTS AND DISCUSSION

3.1 X-ray Diffraction:

The XRD spectra of TiO_2-ZnO nanocatalyst is shown in figure 2. A series of characteristic peaks are noted in the XRD pattern at 2Θ =25.14, 31.13, 38.08, 48.12, 54.43 and 62.67 for TiO_2-ZnO nanocatalyst which is related to (101), (100), (004), (200), (105) and (204) crystallographic plane of anatase TiO_2 and wurtzite ZnO respectively..The mean crystallite size was calculated from the full width at the half maxima of the diffraction peak by the Scherrer's equation(eq.1)

$$D_p = K\lambda / \beta\cos\Theta \quad (1)$$

Where, D_p is the crystallite size in nm, K is the shape factor, λ is the wavelength of X-ray in A^0, β is the full width at half maximum and Θ is the Bragg's angle. The size of the crystallite was found to be 35.5 nm.

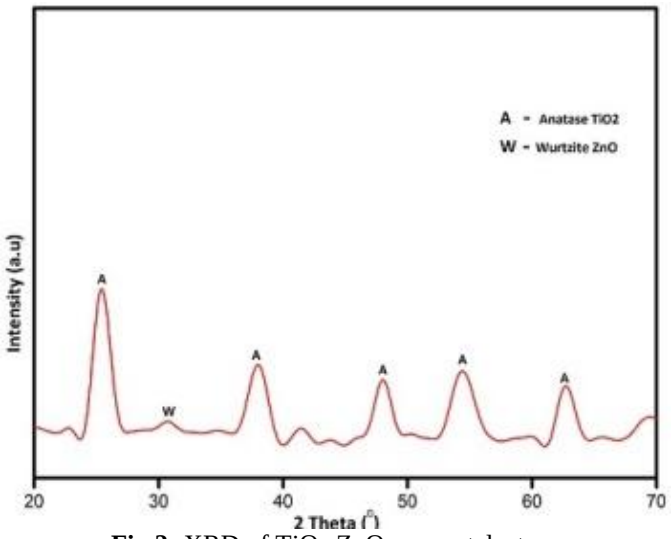

Fig.2: XRD of TiO_2-ZnO nanocatalyst.

3.2 Scanning Electron Microscopy

The SEM image of TiO_2-ZnO nanocatalyst is shown in figure 3. The SEM analysis shows irregular size of nanocomposite particles with a strong tendency to agglomerate. TiO_2 and ZnO particles in the composite couldn't be differentiate due to same electron density of Ti andZn.

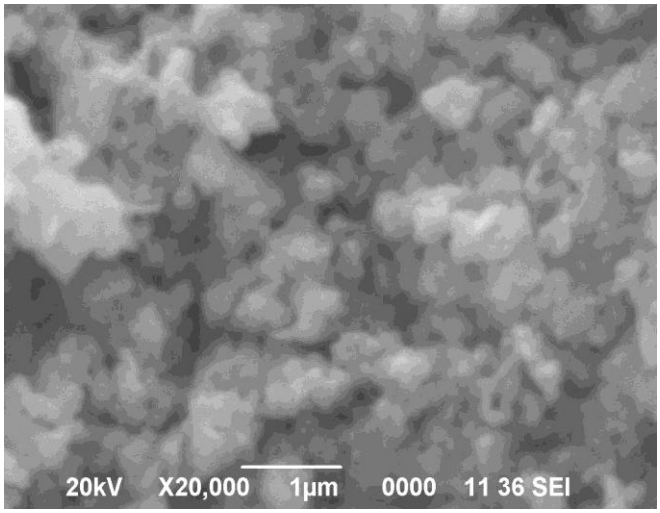

Fig.3 SEM of TiO_2-ZnO nanocatalyst

3.3 FT-IR

FTIR analysis was done in the range of 4000-400 cm^{-1}(fig.4). The IR spectra of TiO_2-ZnO nanocatalystgives a broad peak at 3383 cm^{-1} corresponding to stretching vibration of O-H group. The absorption peak at 2918 and 2858 cm^{-1} are assigned to C-H stretching vibration. The peak at 1619 cm^{-1}results from C=O stretching vibration. The characteristic peaks at 721 and 475cm^{-1} are due to Zn-O stretching and Ti-O stretching respectively.

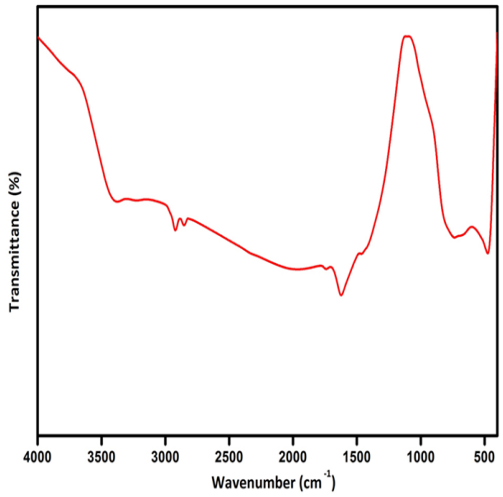

Fig.4 FT-IR spectra of Ti02-ZnO nanocatalyst

3.4 Conversion of FAME (Fatty Acid Methyl Ester) by ^{1}HNMR

The conversion of Thevetia Peruviana oil into fatty acid methyl ester (biodiesel) was analysed by ^{1}HNMR (fig.5). Percentage of biodiesel conversion was determined by following equation (Eq2.) [34].

$$C\ (\%) = 100 \times (2A_{ME}) / (3A_{CH2}) \qquad (2)$$

Where C denotes percentage of conversion of triglycerides to fatty acid methyl esters, A_{ME} is the integration value of methyl ester protons (~3.6ppm) and A_{CH2} is the integration value of methyl protons (~2.3ppm). The percentage of biodiesel conversion was found to be 94.11%.

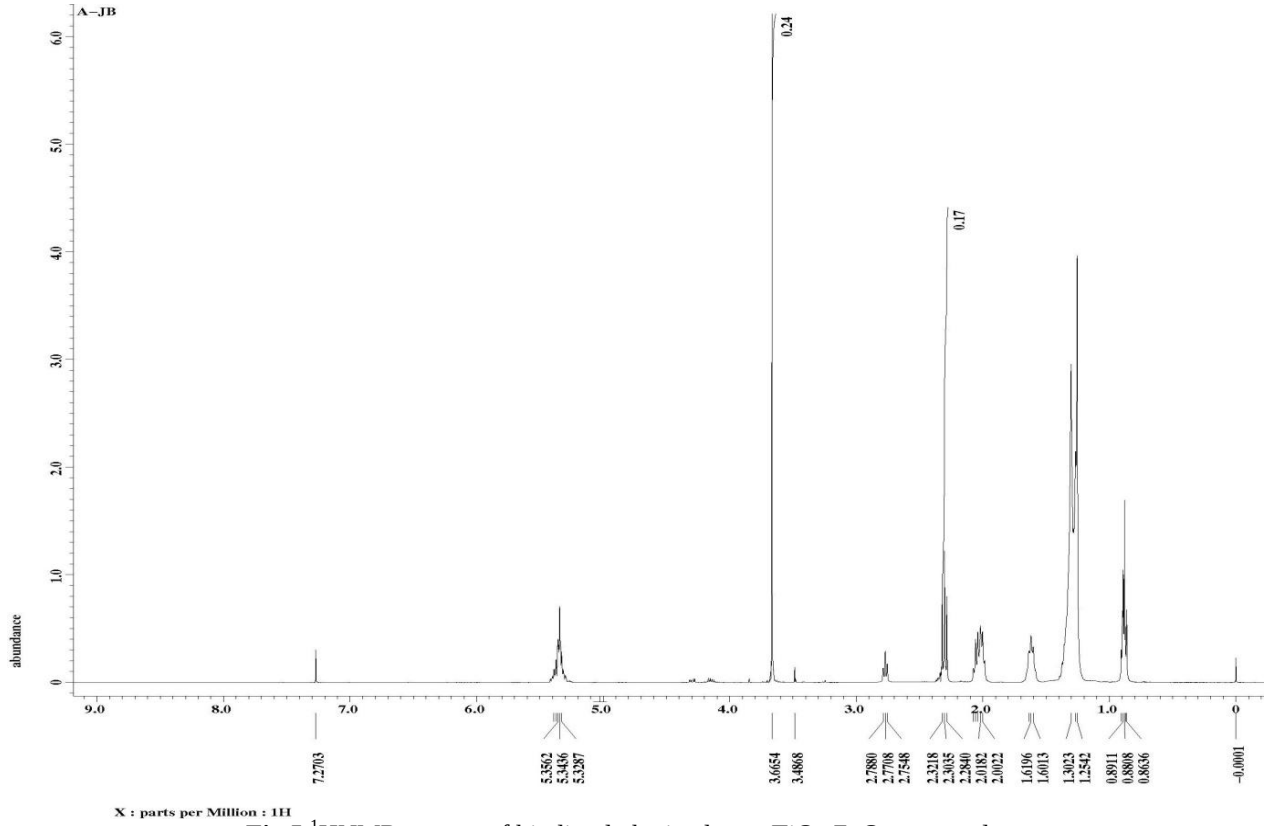

Fig.5 ^{1}HNMR spectra of biodiesel obtained over TiO_2-ZnO nanocatalyst

4. CONCLUSION

The current work explores the synthesis of TiO_2-ZnO nanocatalyst for the efficient production of biodiesel using Thevetia Peruviana oil seeds as a feedstock. Biodiesel conversion of 94.11% was obtained using oil and methanol in 1:6 molar ratio, catalyst concentration of 6 wt% (with respect to oil) for 5 hours at 65^0C. This enhanced activity of the $Ti0_2$-ZnO nanocatalyst could be ascribed to the large surface area and site of exposure during the transesterification reaction and the creation of defects due to the incorporation of Zn ion on the TiO_2 lattice. The TiO_2-ZnO nanocatalyst shows good catalytic performance and hence can be used for large scale biodiesel production from Thevetia Peruviana oil. The reaction parameters and kinetics of transesterification have to be studied to develop an ideal biodiesel production process.

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