SYNTHESIS OF BIODIESEL FROM NEEM OIL VIA TRANSESTERIFICATION PROCESS USING MG DOPED TITANIUM DI OXIDE

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Abstract

The Mg doped TiO_2 is synthesized by sol-gel method. The prepared solid nanocatalyst was characterized by XRD, FT-IR . The catalyst showed the highest yield of 89% for transesterification reaction at 65ºC, 6 hour with 150mg catalysts loading. The reusability of the catalyst was moderate and future studies focusing on regeneration and enhancing the reusability of the catalyst are recommended.

Introduction

Biodiesel fuel is well known as a biodegradable, renewable, nontoxic, and eco-friendly that can substitute petro-diesel perfectly(Meng et.al 2013)which can be used directly or diesel mixture in engine with little changes(Dehkordi and Ghasemi et al 2012). The majority of world's energy is supplied through petrochemical sources, coal and natural gases. New renewable sources have been widely studied due to the reduction of petroleum reserves and increase in environmental and health concerns [1]. The demand of petroleum –based fuels also increases with increase in the industrialization and motorization of the world. So there is an alternate solution is need to alleviate all the problems .Biodiesel is the opt way to rectify the fuel demand and the environmental issues produced by petroleum productions, bio-diesel is also reduce the dependency on natural resources and greenhouse gas emissions [2]. Conversion of crude oil, coal and natural gas to fuels and chemical feed stocks, production of a variety of petrochemical and chemical products and emission control of CO, hydrocarbons, and NO, are rely on catalytic technologies.[3]. The application of nanotechnology in the domain of harmful dye degradation, pesticide degradation, Water purification, Biodiesel synthesis, in drug synthesis are highly markable. The particle size of the catalyst is one of the most important factors for their catalytic activity [4]. Various Nano catalysts have been investigated for biodiesel production such as Wen et al.Catalytic technologies are critical to present and future energy, chemical process and environmental industries. .[5-7].The main objective of this work is to synthesize the maximum amount of biodiesel in the presence of Mg doped TiO_2 nanocatalyst, here the efficacy of reusability of nanocatalyst also analysed.

2.Methods

2.1Materials and Methods

Refined Neem oil (NO) was purchased from local market. Methanol (>99% purity) and all other materials were of analytical grade purchased from E-Merck, India and were used as received without purification. Mg doped TiO_2 was prepared by sol-gel method. Titanium tetra-n-butoxide[ti(o-Bu)4]Magnesium nitrate obtained from E-merck AR grade, were used as titanium and magnesium sources for preparing Pure TiO_2 (anatase form) and Mg^{2+} doped TiO_2 photocatalysts. All other chemicals and reagents are of merck(India) Analytical grade.

Initially 21ml of Titanium tetra-n-butoxide[ti(o-Bu)4] was dissolved in 80 ml of absolute ethanol (100%) and the resulting solution was stirred vigorously. Then 2ml of water and 0.5 ml of acetic acid 50% were added to another 80ml of ethanol to make ethanol-water-acetic acid solution. The later solution was slowly added to the ti(O-Bu)4 ethanol solution under vigorous stirring. When the resulting mixture turned to sol, the magnesium nitrate solution was added drop-wise. The resulting transparent colloidal suspension was stirred for more than 2 hours and aged at 25°C until the formation of gel. The gel was dried at 70°C in Vacco pressure of 600psi and then ground. The resulting powder was calcined at 400°C for 2 hours in 50°C increments for every 30 minutes until reaching 400°C after calcination period, the furnace was allowed to cool for 2 hours. The calcined powders were crushed using pestle and mortar under similar conditions in attempt to produce powders with similar fineness and particle size distribution.

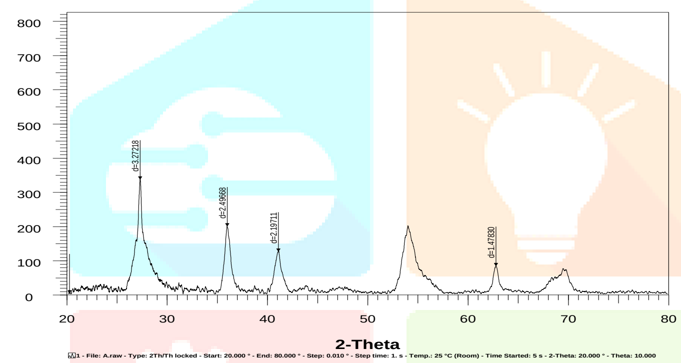
2.2Transesterification of Neem oil

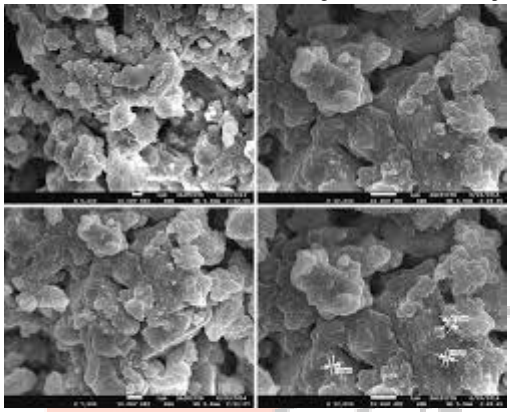
The production of biodiesel from ethanol and Neem oil has been used in the transesterification process. Mg doped Tio_2 have been selected as catalyst. First 20 ml of ethanol was mixed with Mg doped Tio_2 with different ratio (0.50mg -300mg).This is an exothermic reaction.so the mixture would get hot. Then the mixture was preheated about 65°C. Then the mixture was shaken for 5 minute in a glass beaker. After completion of the methanolysis reaction (6 hour), the catalyst was recovered from the reaction mixture by centrifugation and excess methanol was recover in distillation unit. When the product was cooled, an oil phase clearly separated from a glycerol phase. The top oil phase i.e. biodiesel was collected. The percentage of biodiesel yield was defined as

$$\text{Yield of Biodiesel} = \frac{\text{volume of Biodiesel (V1)}}{\text{Volume of Neem oil(V2)}} \times 100$$

2.3Characterization of Catalyst

The crystallinity was determined by XRD using Bruker D8 advance X ray diffractometer equipped with Cu kα (λ=1.54Å) source (applied voltage 40kV, current 40mA) about 0.5g of the dried particles were deposited as a randomly oriented powder, onto a Plexiglas sample container, and the XRD patterns were recorded at angles between 20º and 80º with a scan rate of 1.5º/min .The crystallite domain diameters(D) were obtained from XRD peaks according to the Scherrer's equation $D=(0.89\lambda/\Delta W \cos\theta)$. The XRD patterns Confirms particle size are at nano level . The SEM images were collected with a JEOL 630-F microscope. Before measurements, samples were dispersed on a steel plate surface and coated with Pt metal. FT-IR spectra of pure TiO2 and Mg doped TiO2 given in fig(2a,2b),have shown peaks corresponding to stretching vibrations of O-H and bending vibrations of adsorbed water molecules around 3226.11cm^{-1} and 1629-1382 cm^{-1} respectively. Also, a peak was observed around3406 cm^{-1} which might be attributable to C-H vibrations likely due to acetate methyl groups. The broad band below 999.66cm^{-1} is due to Ti-O-Ti vibration. A peak has been observed at 1382 cm^{-1} which can be assigned to Ti-O-Mg vibration.





Fig(1)XRD images of Mn doped TiO_2 Fig(2)SEM images of Mg doped TiO_2

2.4 Characterization of oil

The quality of soybean oil is expressed in terms of the physicochemical properties such as density, acid value, flash point, Moisture content, Ash content, viscosity etc. These quality checking process are carried out by suitable methods.

3. Results and Discussion

3.1Density.of biodiesel

5ml clean empty measuring jar is weighed(W1), Water is used to the reference solution in this process so measured the weight of water with measuring jar(w2) and measured the weight of biodiesel with measuring jar is noted(w3).Measuring the weight of biodiesel with measuring jar process is repeated at least 5 times, then the average is calculated. Here the density is calculated with the formula Density = Mass/volume, the values of weight of measuring jar with biodiesel are listed in Table(1).The calculated density of the biodiesel from the below value is 0.9061gm/ml.

Table(1) Density

S.NO	Weight of Measuring jar with Biodiesel(g)
1.	33.0639
2.	32.9638
3.	32.9626
4.	32.9611
5.	32.9602
6.	W1=28.4514g
7.	W2=33.3440g

3.2 Determination of acid Value

The acid value of the biodiesel is determined by titration. First a blank titration is carried out between 0.1N NaOH and 50 ml of alcohol (Blank) ,then the above titration is carried out with 20ml of biodiesel , phenolphthalein indicator is used for both titration.

The two titrated values are used to determine the acid value by using the below formula,and the calculated acid value of biodiesel is0.6705mg.

$$\text{acid value} = \frac{(A-B)X(0.1)X\ N}{W}$$

Here A=Blank Value, B=Titrate Value, N=Molecular weight, W= biodiesel weight

3.3 Determination of flash point

Flash point is the temperature at which the fuel will ignite when exposed to spark of flame, and it is found as 70°C.

3.4 Determination of viscosity

Viscosity of the biodiesel is determined by Oswald viscometer, and it was found to be in the range of 40.05.

3.5 Determination of ash content

Ash content is the non-volatile inorganic matter of a compound which remains after subjecting it to a high decomposition temperature. It is the measure the amount of metals contained in the fuel. A known weight of the sample in a porcelain crucible is heated over the burner till combustion is complete leaving behind as a residue(1hr). Weight of empty crucible(w1)g, Weight of crucible+ sample(w2),(before heating) Weight of crucible + ash (w3)(after heating) and the ash content value is determined from the below formula, determined ash content is 0.05gwhich is equal to synthesized biodiesel.

$$\text{Ash content} = \frac{\text{Weight of ash}}{\text{Weight of sample}} X100$$

3.6 Determination of Moisture content

Moisture content is determined by Over drying method. Weight of empty crucible(w1)g, Weight of crucible+ sample(w2),(before heating) Weight of crucible + sample(w3)(after heating) and the ash content value is determined from the below formula, and the calculated moisture content is 96.4g

$$\text{Moisture content} = \frac{(w2-w3)}{(w2-w1)} X100$$

Optimization of reaction conditions on the transesterification of Neem oil

3.7 Influence of amount of catalyst

The effect of the amount of catalyst on biodiesel yield was investigated by varying the load from 0.50-200mg .The reaction was carried out at 65ºC for 6 hour with a methanol to oil molar ratio of 12:1. It was found that the yield of biodiesel was initially increased from 55% to 93% with amount of catalyst was increased from 0.50-200mg and a slight fall in the conversion was observed at 150 mg. At higher catalyst loads, the reaction mixture may become more viscous which resists the mass transfer in the liquid–liquid–solid system and hence, results in the decline of biodiesel yield. The catalytic activity of our catalyst was compared with that of other similar catalyst. It shown at Fig(3)

3.8 Influence of time

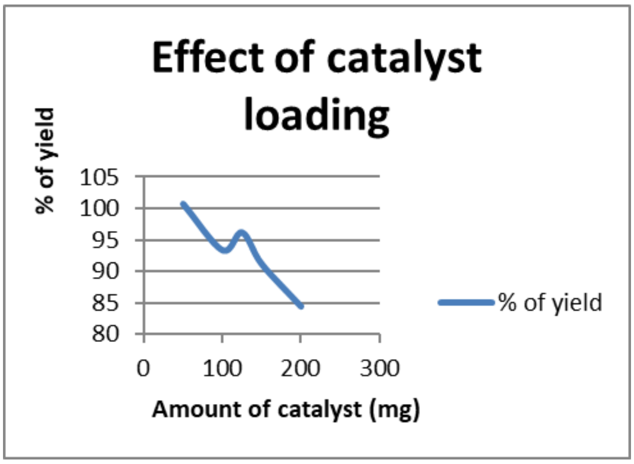
The yield of biodiesel is increased with reaction time from 2-10 hours,the yield is increased upto 6hour ,further increasing of reaction time is decreases yield of the biodiesel .So the optimum reaction time is 6 hours.It is shown in fig(4)

3.9 Influence of RPM

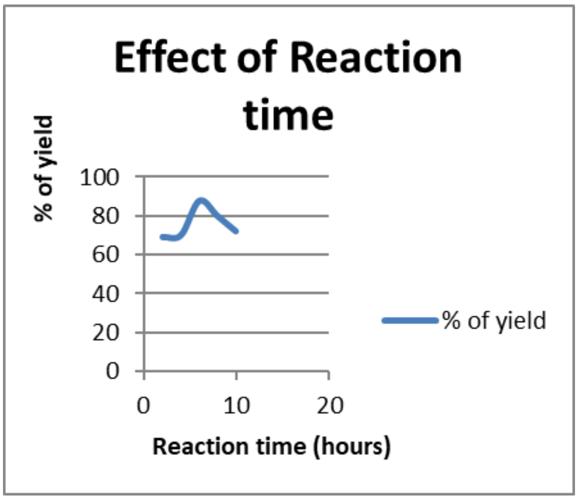
The Yield of biodiesel is decreased by increased rotation per minute . The RPM is increased from 100-500RPM .The maximum yield is obtained at 100RPM, at 6 hours of reaction time at constant amount of catalyst 150mg. It is shown in fig(5)

3.10 Reusability of the catalyst

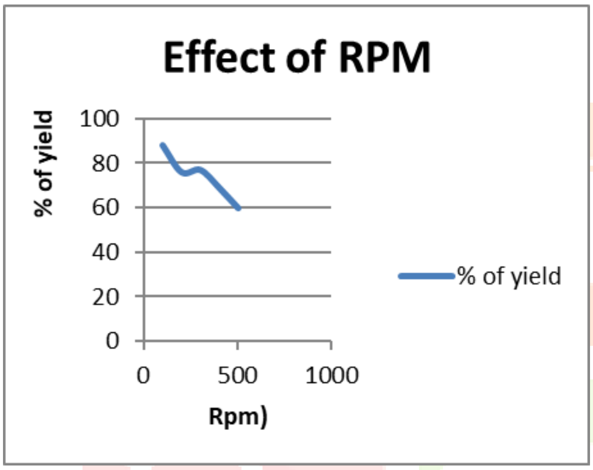
From economic point of view, the reusability the catalyst is of great importance for industrial application. As shown in figure(6), the recyclability efficiency of the calcined Mg doped TiO2 was investigated by performing the transesterification steps for several runs. To evaluate the reusability, the supernatant biodiesel and glycerol layers were discharged and the solid catalyst was left in the flask under the optimum conditions. Same amount of fresh soybean oil and methanol was added into the flask and performed transesterification reaction again. The catalytic activity of calcined Mg doped TiO_2 decreased sharply with in 5 runs from 89% reduced to 70% respectively as shown in figure 6. Because the catalyst particle was crushed by strong stirring and the powder like small particles were discharged with supernatant glycerol, no further experiments were conducted.



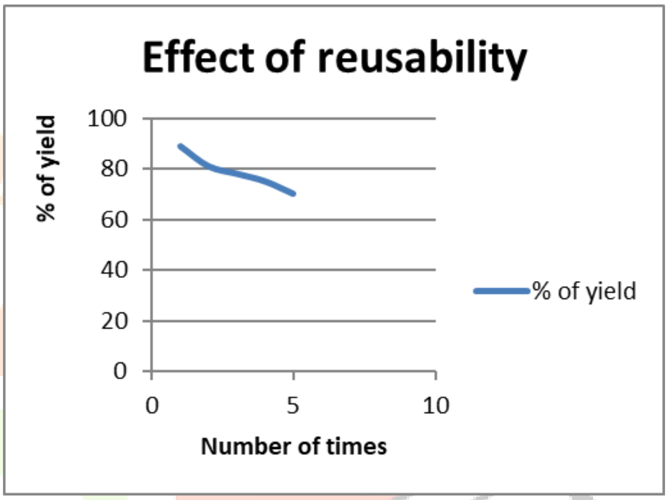
Fig(3) Effect of catalyst



Fig(4) effect of reaction time



Fig(5) Effect of rpm



Fig(6) Effect of reusability

4. CONCLUSION

Mg doped Tio_2 tested as solid nanocatalyst in transesterification of Neem oil in batch reactor systems. The prepared solid catalyst was characterized by XRD, FT-IR . The catalyst showed the highest yield89% for transesterification reaction at 65ºC, 6 hour with 150mg catalysts loading. The reusability of the catalyst was moderate and future studies focusing on regeneration and enhancing the reusability of the catalyst are recommended.

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