

Preparation of Zirconia Supported Basic Nanocatalyst: A Physicochemical and Kinetic Study of Biodiesel Production from Soybean Oil

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Abstract: Zirconia supported cadmium oxide basic nanocatalyst was prepared by simple co-precipitation method using aq. ammonia as precipitating reagent. The catalyst was characterised by X-ray diffraction, scanning electron microscopy (SEM) and transmission electron microscopy technique (TEM), Brunauer-Emmett-Teller surface area measurement (BET), temperature program desorption (TPD-CO₂) etc. The transesterification of soybean oil with methanol into biodiesel was catalysed by employing zirconia supported nanocatalyst. Kinetics of transesterification of oil was studied and obeyed the pseudo first order equation. While, the activation energy (E_a) for the transesterification of oil was found to be 41.18 kJ mol⁻¹. The 97% yield of biodiesel was observed using 7% catalyst loading (with respect of oil), 1:40 molar ratio of oil to methanol at 135°C.

Key words: nanocatalyst, zirconia support, biodiesel, heterogeneous catalyst

1 Introduction

Biodiesel is key alternatives of energy to non renewable energy resources. It is ecofriendly, biodegradable and renewable resources of energy accompanied with high lubricity, high flash point and better oxidation stability. Traditionally, biodiesel has been produced by the basic homogenous catalyst like NaOH, KOH, etc. by transesterification of oils with alcohol. The homogenous catalyst showed greater activity, but it suffers with some problems like biodiesel separation, saponification etc.

In order to overcome the demerits like leftovers of fatty materials, the heterogeneous catalysis were used. These are efficient methods for production of bio-diesel, because of the recyclability of catalyst, environment friendly, non corrosive, avoids saponification of fatty materials and easily separable etc.¹⁻⁴.

There has been much more heterogeneous catalysts were studied for transesterification of oil likely, metal oxide CaO⁵, clay⁶, mixed metal oxide supported on Al₂O₃⁷, lanthanum doped Zn-Al mixed oxide⁸, Mg-Al hydrotalcite material⁹, chitosan¹⁰, heteropolyacid supported on ZrO₂ support¹¹, KI/Al₂O₃¹², Cao/Al₂O₃¹³, ZrO₂-SBA-15 acid catalyst¹⁴, zinc glycerate¹⁵ etc..

Herein, the ZrO₂ supported cadmium oxide nanocatalyst

was prepared by co-precipitation method and analysed by diverse instrumental tools like; TGA, SEM, TEM, XRD, and TPD-CO₂ etc. The catalytic efficiency of catalyst was studied by transesterification of soybean oil to biodiesel. We optimised the reaction parameter like temperature, time, catalyst and molar ratio of oil to methanol etc. The kinetics of transesterification of oil was studied by determining the rate constant (k) and activation energy (E_a) at different temperature.

2 Experimental Section

2.1 Materials

Cadmium nitrate (AR), zirconium nitrate (AR) from M/s Merck chemicals Pvt. Ltd., Mumbai, methanol, hexane, methyl salicylate from M/s Himedia chemicals Pvt. Ltd. All chemicals were AR grade while refined soybean oil (Fortune) was procured from local market.

2.2 Catalyst preparation

The catalyst was prepared by (co-precipitation method) dissolving an equimolar mixture of both metal nitrates into 250 ml beaker with minimum amount of distilled water.

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The ammonia solution (30%) was added dropwise into well stirred mixture of metal nitrate, till a pH 9-10 was obtained. The precipitate was filtered and washed with distilled water to ensure a neutral pH. The product was dried into oven at 105°C for 6 h. Finally, the precipitate was crushed and calcined at 650°C for 3 h.

2.3 Catalyst characterisation

Thermo gravimetric analysis (TGA) was carried out using Perkin Elmer STA 6000 model. It was heated at 10°C/min initially from 30°C under the 20 ml/min flow of nitrogen. Surface morphology of the catalyst was studied by field emission Gun-Scanning electron microscope (FEG-SEM JSM -7600F model). The catalyst structure and crystalline size of catalyst was studied by X-Ray diffraction over Shimadzu XRD (6100) instrument coupled with CuK α ($\lambda = 1.5405\text{\AA}$) source of radiation. While diffraction pattern scans over the 2θ value ranging from 20 to 90°. Transmission electron microscopy (TEM) images were recorded on Philips, model Tecnai 20. The basic site of catalyst was analysed by temperature program desorption (TPD-CO₂) using Thermo electron (TPD/R/O 1100) instrument. Firstly the surface of the catalyst was cleaned by helium gas for 5 min and started absorption of CO₂ gas with 20 ml/min at 50°C for 200 min on active basic sites of the catalyst. Then, finally desorption of CO₂ was carried by means of a helium gas with a flow of 10 ml/min, temperature started at room temperature to 1000°C and hold for 5 min. While the surface area of the catalyst was measured by N₂ adsorption - desorption using BET (Brunauer-Emmet-Teller) method, using ASAP 2010 (Micromeritics) instrument.

2.4 Transesterification reaction

The transesterification was performed in 250 ml stainless steel autoclave equipped with a cooling system. The 7% (with respect to oil) of catalyst, 1:40 molar ratio of oil to methanol were fed to the reactor with reaction temperature varied between 100-135°C for 3 h. The reaction product was analysed by Gas chromatography of Thermo scientific (Chemito GC1000) equipped with flame ionisation detector by using DB-05 capillary column. The initial oven temperature was 100°C holds for 2 min raised 8°C/min to 270°C, where 250°C and 260°C are the detector and injector temperatures. Nitrogen was used as carrier gas. Finally, the product was characterised by GC-MS analysis.

2.5 Reaction kinetics

Usually kinetics of transesterification of oil considered as a pseudo first order reaction, due to excess of alcohol employed in reaction as stoichiometrically required (3:1) alcohol to oil ratio. The effect of time on conversion of oil to biodiesel was obtained and first order rate constant with activation energy was calculated by the following equation (1) and (2) respectively.

$$-\ln(1 - X) = k t \quad (1)$$

$$k = A.e^{-E_a/RT} \quad (2)$$

While, X is the conversion of oil to biodiesel, t is the reaction time, k is first order rate constant (min⁻¹), E_a is the activation energy (kJ mol⁻¹), A is pre-exponential factor (min⁻¹), R is gas constant (8.314 × 10⁻³ kJ K⁻¹ mol⁻¹) and T is the reaction temperature (K).

2.6 Study of flash point and pour point of biodiesel

The flash point of biodiesel was studied by filling test cup (15 ml) with biodiesel and fit into flash point apparatus equipped with thermometer and heating coil. The flame of fire was sliding over the surface of biodiesel under heating condition and short noisy flash was observed over the surface i.e., the flash point of compound.

While pour point of the compound was determined by pour point apparatus equipped with cooling machine. The 10 ml of product was poured into test tube and put into the chamber along with thermometer and check the pour point of compound.

3 Results and discussion

3.1 Catalyst characterisation

The XRD of nanocatalyst was shown in Fig. 1; it showed peaks at a 2θ value of 30.15°, 35.13°, 50.56°, 60.14° appeared due to ZrO₂ oxide having (101), (110), (200) and (211) planes respectively of tetragonal phase. Meanwhile diffraction peaks at 33.65°, 38.44°, 55.42°, 66.05° and 69.39° depicts the (111), (200), (220), (311) and (222) planes of cadmium oxide^{16,17}. The average crystalline size of catalyst was determined by Scherer's equation, $D = 0.9\lambda/\beta\cos\theta$ (where D is average crystalline size, λ is wavelength of X-ray beam of CuK α , β is full width at half maximum of diffraction peaks, θ is Bragg's angle) and was found within

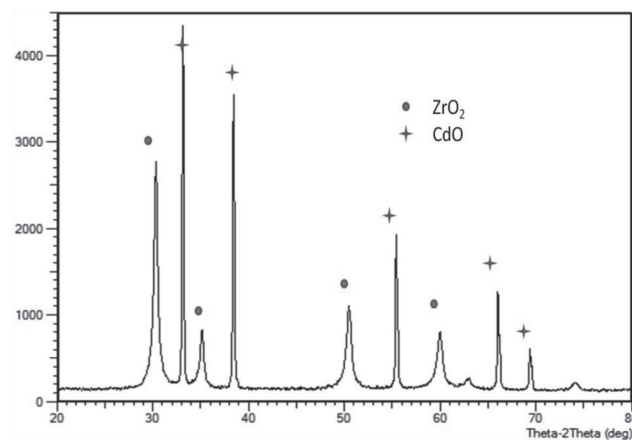


Fig. 1 XRD of CdO/ZrO₂ mixed metal oxide.

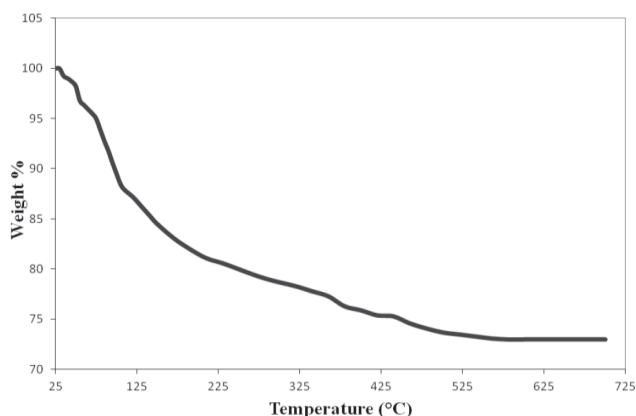


Fig. 2 DSC-TGA of CdO/ZrO₂ mixed metal oxide.

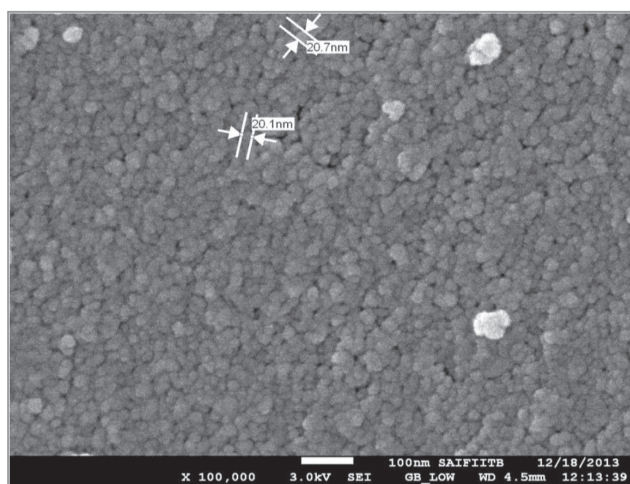


Fig. 3 SEM image of CdO/ZrO₂ mixed metal oxide.



Fig. 4 TEM image of CdO/ZrO₂ mixed metal oxide.

range of 58 nm. The thermal stability of the catalyst was studied (Fig. 2). It showed a 15% weight loss observed from 30°C to 150°C due to surface moisture. While 12% weight loss over the 150°C to 650°C attributed to the formation of metal oxide and no distinct loss in weight was observed between 650°C to 700°C. The FEG-SEM (Fig. 3) and TEM images (Fig. 4) clarify that nanocatalyst was spherical in shape.

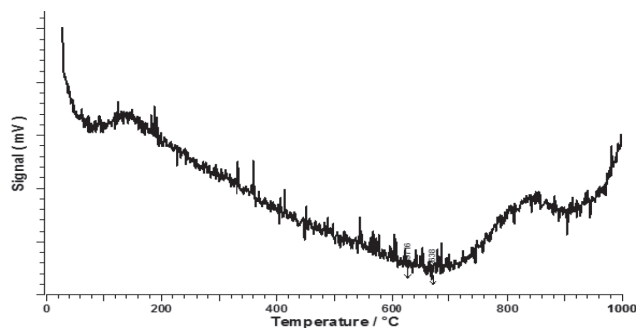


Fig. 5 TPD/CO₂ of CdO/ZrO₂ mixed metal oxide started from RT to 1000°C temperature.

Table 1 Effect of calcination temperature on surface area and basicity of catalyst.

Calcination temperature	BET area (m ² /g)	Basicity mmol/g
600°C	105	0.68
650°C	76	0.97
700°C	63	1.31

The TPD-CO₂ graph (Fig. 5) shows that the weak basic sites over the 100-150°C temperature range, while strong basic site over the 300-700°C was observed. The basicity of mixed metal oxide was found to be 1.31 mmol/g. The calcination temperature is the influencing parameter on the specific surface area of catalyst (shown in Table 1).

3.2 Transesterification study

Transesterification is reversible reaction; there are certain parameters which shifts the equilibrium to the forward direction. The different parameters namely temperature, time, catalyst and molar ratio of methanol to oils etc. and its impact on transesterification was studied.

3.2.1 Reaction temperature

Usually, heterogeneous biphasic catalytic system required higher temperature and pressure for higher conversion of biodiesel. The effects of temperature on biodiesel conversion by nanocatalyst were studied over the range of temperature of 100°C to 135°C. The conversion of biodiesel was increased with temperature from 100°C to 135°C with a 1:40 molar ratio of oil to methanol at 7% catalyst loading as evident from Fig. 6. The 97 % conversion of biodiesel was observed at 135°C after 3 h.

3.2.2 Reaction time

The impact of reaction time on catalytic conversion of biodiesel was studied. Figure 7 showed effect of reaction time on catalytic transesterification with a 1:35 molar ratio of oil to methanol at 6% (with respect of oil) catalytic loading over the range of 100°C to 120°C temperature. The result proved that biodiesel yield increased with time (1 to 5 h) and temperature (100 to 120°C).

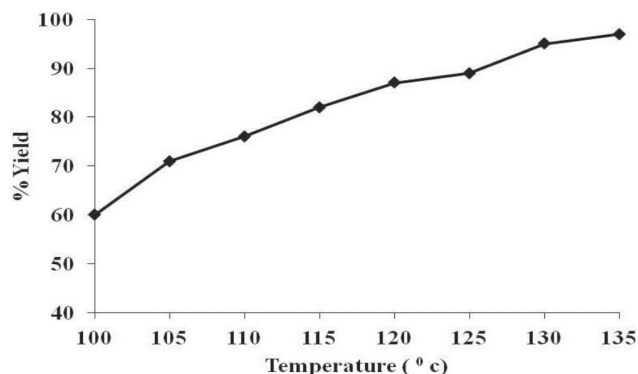


Fig. 6 Effect of temperature on catalytic conversion of biodiesel, 1:40 molar ratio of oil: methanol, 7% catalyst loading, for 3 h.

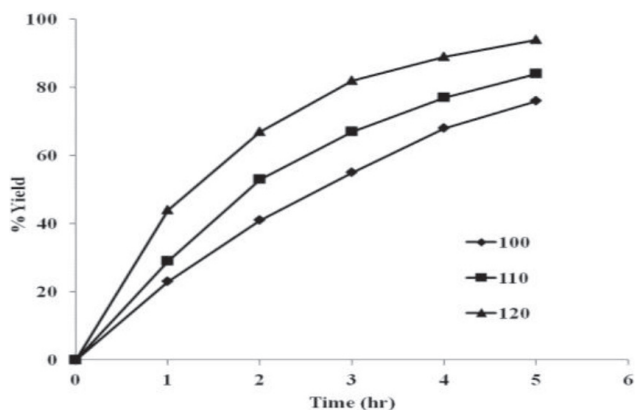


Fig. 7 Effect of time on catalytic conversion of biodiesel at 1:35 molar ratio of oil: methanol, 6% catalyst loading at 100°C, 110°C and 120°C temperatures.

3.2.3 Ratio of oil to methanol

The oil to methanol molar ratio played important role in catalytic transesterification of oil to biodiesel. Normally 1:3 molar ratio is required for transesterification of oil, but excess of alcohol imparts on shifting of equilibrium towards forward direction (transesterification being reversible reaction) in order to achieve higher conversion. The excess of alcohol enhances the rate of reaction along with separation of catalyst from reaction mass^{18–20}. The transesterification were carried at a variable molar ratio of oil to methanol from 1:30 to 1:40. **Figure 8** showed that the conversion of biodiesel was enhanced with a molar ratio from 1:30 to 1:40; it showed 95% yield at 1:40 molar ratio. Enhancement in the transesterification reaction was observed by increase in molar ratio of oil to methanol.

3.2.4 Effect of calcinations temperature and catalyst loading

The effects of calcination temperature and catalyst loading on biodiesel conversion were studied are shown in **Fig. 9**. The biodiesel conversion enhanced up to 80% with

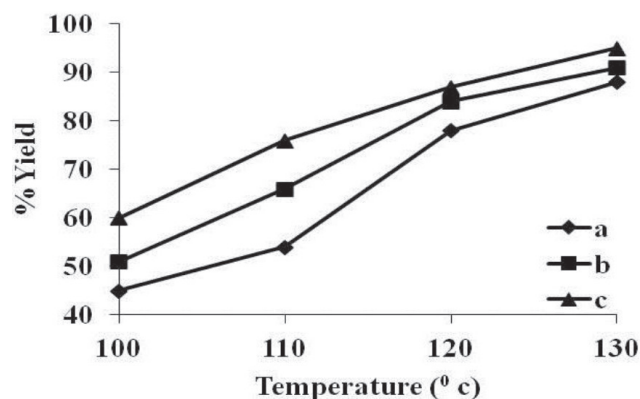


Fig. 8 Effect of molar ratio of oil: methanol on biodiesel conversion a) 1:30 molar ratio b) 1:35 molar ratio c) 1:40 molar ratio, 7% of catalyst loading for 3 h.

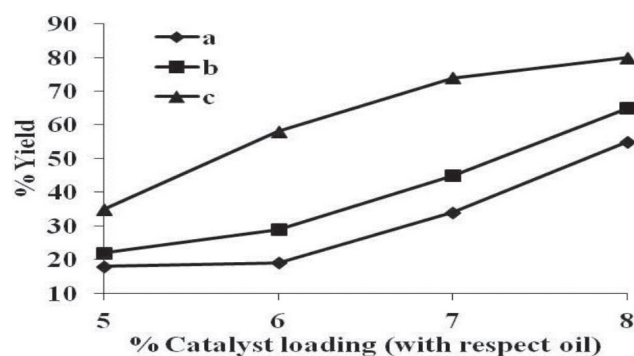


Fig. 9 Effect of catalyst calcination temperature and its loading on biodiesel (a) 600°C calcination temperature (b) 650°C calcination temperature c) 700°C calcination temperature 1:35 molar ratio of oil: methanol at 110°C for 2 h.

calcinations temperature and catalyst loading from 5% to 8% (with respect of oil) at a temperature 110°C with 1:35 molar ratio of oil/methanol (**Fig. 9**). Basicity of the catalyst was increased with calcination temperature, it might be due to enhancement in active basic sites of the catalyst (shown in **Table 1**); which ultimately imparts in activity of the catalyst (**Fig. 9**).

3.2.5 Recyclability of catalyst

The catalyst recyclability was studied in order to check the catalytic activity for transesterification. The catalyst was recovered from the reaction mass by washing with hexane followed by drying in oven at 100°C and calcined at 700°C. The recyclability study of first case catalyst was carried for 5 consecutive times, which showed 95%, 95%, 94%, 92% and 88% biodiesel yield without any significant loss. The minor decrease in conversion was might be due to deposition of glycerol, the reaction intermediate and biodiesel, which blocked the active sites of the catalyst (**Fig. 10**).

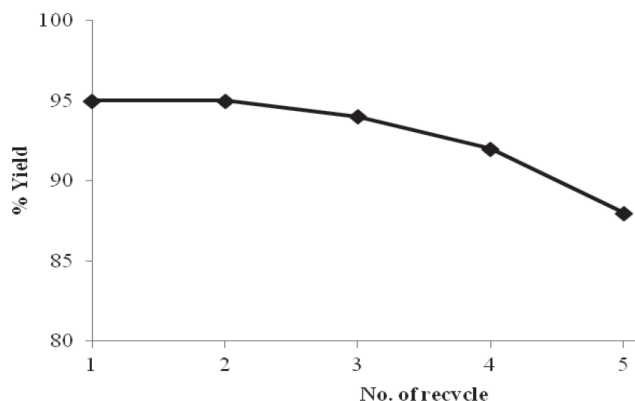


Fig. 10 Study of recyclability of catalyst on biodiesel yield at 1:40 molar ratio of oil: methanol, 7% catalyst loading at 130°C for 3 h. (Washing of catalyst with hexane followed by drying in oven at 100°C).

3.2.6 Kinetic study

The thermal transesterification reaction of oil was accompanied with three steps reported by Kusdiana and Saka (2001) and Fukuda *et al.* (2001). Kinetic study of transesterification of oil has been studied by considering the single step reaction instead of intermediate steps like, diglyceride and monoglyceride. The catalytic transesterification of oil in presence of excess of alcohol obeyed pseudo first order kinetics^{21, 22}. The kinetics of transesterification of oil catalysed by mixed metal oxide was determined at different temperature and respective graph between $-\ln(1-X)$ vs Time (shown in Fig. 11). The rate constant of reaction at different temperature shown in Table 2.

The graph of $-\ln(1-X)$ vs Time for transesterification of oil was showed linear relationship, which justify pseudo first order kinetics of the reaction. Meanwhile activation energy of transesterification reaction was determined by Arrhenius equation. The graph of $\ln k$ vs $1/T$ (shown in Fig. 12) and activation energy (E_a) was found to be 41.18 kJ/mole. It is observed to be kinetically controlled reaction as evident from activation energy determination.

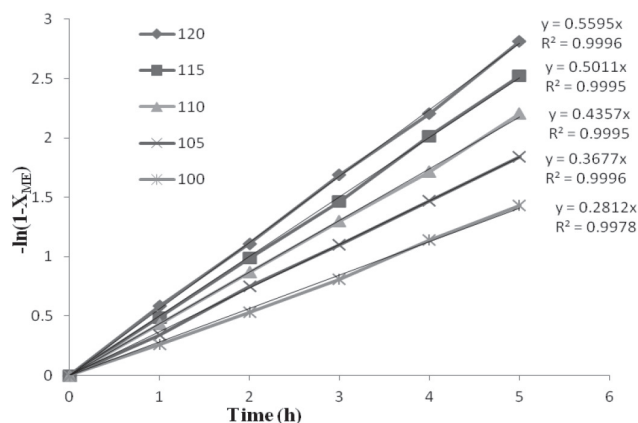


Fig. 11 Plot of $-\ln(1-X)$ vs Time at different temperature with 1:35 molar ratio of oil to methanol, 6% catalyst loading.

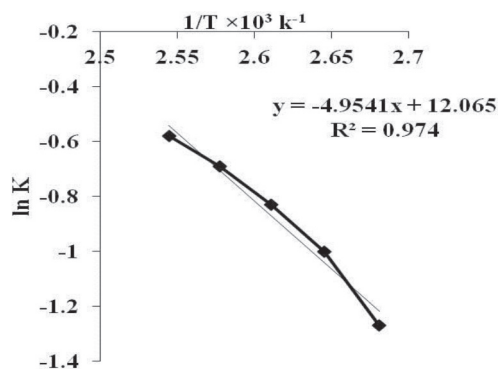


Fig. 12 Arrhenius plot $1/T$ against $\ln k$ of transesterification of oil by methanol.

3.2.7 Physicochemical properties of biodiesel

The physicochemical properties like, acid value, flash point, cloud point and FAME content of biodiesel were analysed by American standard (ASTMD standard). The biodiesel has been prepared for physicochemical study such as; the transesterification of oil was performed in 250 ml stainless steel autoclave equipped with a cooling system. The 7% (with respect to oil) of catalyst, 1:40 molar ratio of

Table 2 The rate constant of reaction at different temperature.

Temperature (°C)	100	105	110	115	120
Rate constant (sec ⁻¹)	0.2812	0.3677	0.4357	0.5011	0.5595

Table 3 Physicochemical properties of bio-diesel.

Sr. No	Parameters	Units	Biodiesel	Biodiesel range	Test method
1	Ester content	%	97	96.5	GC-MS
2	Acid value	mg of KOH/g of sample	0.21	0.8	ASTMD664
3	Flash point	°C	167	100 - 170	ASTMD93
4	Cloud point	°C	-1	-3 to -15	ASTMD2500

oil to methanol were fed to the reactor with reaction temperature at 135°C for 3 h. The FAME content in the sample was analysed by GC-MS analysis and found to be with 97% yield. The acid value of biodiesel was 0.21 mg KOH/g of sample, which is within limit of ASTM standard. Meanwhile, flash point and pour point of biodiesel were found to be 167°C and -1°C which are in between the acceptable range of fuel (shown in Table 3).

4 Conclusions

The prepared nanocatalyst was spherical in shape with a 58 nm average crystalline size. It showed an efficient catalytic conversion of biodiesel up to 97% at 135°C. Transesterification of oil showed a pseudo first order reaction Kinetics with activation energy of 41.18 kJ/mole. The basicity of the catalyst was increased with calcination temperature; it may be due to the increase in active basic sites in catalyst, which enhanced the biodiesel yield. Catalyst recyclability was studied for five consecutive times without any significant loss in catalytic activity. The physicochemical properties of biodiesel were found within the range of EN 14214 standards (Shown in Table 3).

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