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# Characterization and Testing of KF/CaO Heterogeneous Catalyst for Biodiesel Production

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The application of heterogeneous catalyst in the production of biodiesel cannot only decline the costs of the separation process but also reduce the cost of biodiesel. The present study has emphasized on the performance evaluation of KF/CaO catalyst for biodiesel synthesis from nonedible Jatropha curcas oil (JCO). The synthesized catalyst was characterized through various analytical methods such as powder X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), $CO_2$-temparature program desorption ($CO_2$-TPD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) spectroscopy, BET surface area (SA) and thermo-gravimetric analysis (TGA). The novelty of this heterogeneous catalyst (KF/CaO) is its reuse without leaching of $Ca^{2+}$. It was observed from experimental study that prepared catalyst reflects high efficiency towards catalytic transesterification activity. Furthermore, the catalyst has admirable stability, making it suitable for use as a solid base catalyst in the manufacture of biodiesel from Jatropha curcas oil with 5.5 percent free fatty acid (FFA). Reusability tests of the prepared catalyst validated that it could be reused up to four times without sacrificingample activity, thereby giving rise to a potentially relevant biodiesel production possibility.

**Keywords:** Free Fatty acids, Jatropha curcas oil, Performance evaluation, Reusability, Transesterification

## 1 Introduction

Increasing demand of energy across the globe is a matter of serious concern. Presently nonrenewable energy sources like petroleum crude, coal, natural gas are contributing more than 80% to meet the energy demand[1]. Volatile oil price, global greenhouse gas emissions, environmental pollution and rapid decline in fossil fuel resources are major drivers of fostering research towards alternative fuels. The production of alternative fuels is essential to meet the world's energy needs. It is worth mentioning that renewable energy sources like wind, geothermal, solar, biomass are also contributing. Among mentioned renewable sources, biodiesel have enormous potential to replace conventional diesel. Biodiesel reduces the dependency on fossil fuels vis-à-vis enhances the global energy security. In comparison to conventional fuels, biodiesel has properties such as non-toxicity, low emission profiles, clean burning fuel, biodegradable and environmentally friendly[2]. Both edible and nonedible feedstock can be utilized to produce biodiesel via transesterification when alcohol and a catalyst are present[3,4]. Among the nonedible sources such as Pongamia, Jatropha, Rubber oil, Castor etc., Jatropha curcas are considered as prominent species for biodiesel synthesis because it is a non-food-based feedstock[5,6]. However, abundant vegetable oils such as olive, sunflower, and corn oil as well as various wastes such as discarded frying oils and animal fats, look to be a profitable choice for biodiesel manufacturing. The process of production of biodiesel involves transesterification, which is alcoholysis of triglycerides in presence of a homogenous or heterogeneous catalyst[7]. At the end of the process the separation of homogeneous catalysts is difficult and expensive because the homogeneous catalysts are molecularly dispersed in the phase as the reactant, products and solvents. However, heterogeneous catalysis is the easily separated at the end of the process.

There have been several studies which uses heterogeneous catalyst in lieu of the transesterification of vegetable oil and alcohol. Teo *et al*[8]. stated the Jatropha oil transesterification with methanol using $CaSO_4/Fe_2O_3$-$SiO_2$. The highest transesterification catalytic activity was achieved at

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12 wt. percent material dosage and 9:1 methanol: Jatropha oil ratio in 4 h at 120°C. Lithium-supported activated carbon shows higher activity towards transesterification of a mixture of nonedible oils such as waste fish oil, bitter almond oil and waste cooking oil[9]. To make biodiesel, KF loaded on MgCaAl hydrotalcite was used to transesterify JCO. While KF loading was 30 wt% with an equal amount of Mg to Ca, the highest conversion of 90% was achieved[10]. CaO after calcination derived from waste material was employed as a catalyst in the synthesis of biodiesel from JCO[11]. For the JCO transesterification, sodium zirconate is an excellent basic catalyst[12].

The development of a KF/CaO catalyst for the production of biodiesel from transesterification of JCO having 5.5% FFA is a novel aspect of this present research work. Although there are a few papers that use a solid-state KF/CaO catalyst to transesterify vegetable oils, nobody was mentioned significant high FFA JCO. The chemical used for KF/CaO catalyst preparation is easily available and lower cost as compared to other catalysts.

In this article, the authors have focused to characterize the property of KF/CaO catalyst to find out the active constituents which is responsible for catalytic activity towards biodiesel production. The said catalyst is not used extensively in case of Jatropha oil. Hence this study will helpful to develop efficient catalyst to produce biodiesel from jatropha oil. Catalyst reuse potential study have also been reported.

## 2 Materials and Methods

JCO was procured from Churu, Rajasthan, India, and had a somewhat higher FFA (5.5 percent). Without additional purification, all reagent grade compounds are employed. Sigma Aldrich in Bengaluru provided the methanol (HPLC grade), CaO, and KF. The wet impregnation approach was used to make the KF/CaO catalyst. In this procedure, 10 g of powder form of CaO was absorbed in a 15–20 ml of KF solution for 1 h (2.5 gm of KF). To widen the support pores, the prepared slurry was placed in a desiccator and coupled to a vacuum pump. Then the slurry was heated to extract the water content in a water bath and then dried for 5 h in hot-air oven at 105°C. Afterwards crushing, the catalyst was calcined in presence of air for 4 h at 600°C at a rate of 5°C/min with the temperature range 105–600°C. A temperature controller (Julabo, USA) and an Ultrapycnometer 1000 (Quantachrome, USA) were used to calculate the real density of catalysts. The probe gas is helium, which has a purity of 99.999 percent[13]. The average of ten consecutive analyses was used to calculate catalyst density. Replacement of the pores with helium gas was executed by purging the sample at 30 minutes. At 32°C, the real density test was performed. Tristar 3000 surface area analyzer (SAA) imported from Micromeritics, USA was applied to determine surface area of prepared catalyst. The BET technique was selected for calculating the surface area of the samples using liquid Nitrogen. The isotherm has been obtained with a relative pressure range of 0.05–0.3, attained straight lines. The surface area was measured through the slope and intercept of the straight line. Before experiments, every samples were degassed at 150°C for 3 h to eliminate gaseous impurities. By applying materials through the KBr pellet technique, the DTGS detector was chosen to recognize the FTIR bands. The Perkin Elmer FTIR instrument (Spectrum GX model) was used to generate FTIR spectra of catalysts with a resolution of 2 $cm^{-1}$ and a range of 400 $cm^{-1}$ to 4000 $cm^{-1}$. About 1 mg of catalyst mixed with 200 mg dried KBr were used to create pellets. Each band was achieved over the course of 50 scans in a transmission mode. Prior to all sampling, background bands were constructed. D-8 advanced X-ray diffractometer imported from M/S Bruker AXS, Germany was used to detect powder X-ray diffraction (XRD). With a step-scan (step size of 0.02°/step, scan speed of 1 sec/step), bands were acquired on a 2θ range of 10 to 75°. Using the JCPDS data bank, the XRD phases were determined using a search match approach. On the ZEISS EVO Series EVO 50 SEM model, SEM investigation of the catalyst was noted. The KF/CaO was layered with the silver sputtering. For estimating particle shape and size of the catalyst, the instrument was kept at 20.0 kV. To examine the elemental composition of catalysts, EDX images of the selected area of materials were taken which is coupled with Scanning Electron Microscopy (SEM).$CO_2$-TPD was carried out by means of Auto Chem 2910 (Micromeritics, USA) to investigate the basicity of the catalyst. Nearly 0.04 gm of powdered KF/CaO catalyst sample was loaded in a quartz “U” spout sample tube and degassed for 1h at 120°C with helium flow rate of 50 ml/min. The gas flow was modified at this temperature after chilling the sample to 45°C. The adsorption of $CO_2$ was performed by means of a 2% $CO_2$ blend with Helium for 45 minutes sequentially. Helium gas was re-streamed at a similar temperature to remove loosely deposited $CO_2$ from the catalyst's surface. Lastly, using helium (50 ml per min), the sample was warmed at flow rate of 10°C per min to 975°C to desorb $CO_2$. TCD was used to determine the amount of $CO_2$ desorbed in the catalyst.

A laser-based particle size analyzer equipment imported from Fritsch GmbH Germany was utilized to determine size of catalyst having resolution of 62 channels (9 mm per 254 mm). Data was collected from 20 scans having measurements stretching from 0.10 – 670.07 µm. TGA-STA 449 F3 Jupiter imported from Netzsch, Germany was used to measure thermal decomposition of KF/CaO in an inert environment at 10°C per min heating rate up to 800°C.

The catalyst was isolated and dried after the initial usage and before each subsequent reuse. To scorch off the carbon-based substantial and reclaim the catalytic activity, the catalyst was calcined at 600°C for 4 h. Then the experimental run were conducted upto 4 cycles at same reaction state as 65°C reaction temperature, 3 h time period, methanol /JCO ratio of 10:1, catalyst wt.% w.r.t. oil of 3%.

## 3 Results and Discussion

### 3.1 Catalyst Characterization

The findings from characterization of the newly prepared KF/CaO catalyst are as follows:

#### *3.1.1 True/real density and BET Surface Area (SA)Analysis*

The true densities of KF/CaO, CaO catalyst were achieved as 2.20 and 2.68 g/cm$^3$ correspondingly. However, the porosity value of KF/CaO, CaO were 21.95% and 20.83%, congruently. The porosity value of KF loading increased from original CaO, may be due to the interaction of $K^+$ and $F^-$ ion due to higher ionic character and helping the process for creating an active center on the surface of the catalyst. This might cause better activity for the biodiesel production.

The isotherms obtained from nitrogen adsorption of CaO and KF/CaO catalyst confirmed that their SAs are 3.48 and 5.99 m$^2$/g separately. The SA of CaO is smaller than the KF loaded on CaO. The increment in SA could be attributed to the rich concentration of -OH on the surface of KF/CaO catalyst and further calcination that opened the locked pores on catalyst surface might have facilitated transesterification.

#### *3.1.2 FTIR Analysis*

The FTIR spectra of CaO and KF/CaO catalysts are presented in Fig. 1. For the support CaO Fig. 1(a), the absorption peaks at (ῡ)3444 cm$^{-1}$ and 1632 cm$^{-1}$ were due to absorbed water and similarly peak at 3421 cm$^{-1}$ was observed in KF/CaO Fig. 1(b) catalyst. In KF/CaO catalyst, the band at 3645 cm$^{-1}$ showed surface hydroxyl group existence. Further another peak on KF/CaO at 3695 cm$^{-1}$ was accountable for the isolated OH group. The catalytic activity may be responsible for this isolated OH group. It was reported that the surface -OH group facilitated transesterification[14].

#### *3.1.3 XRD Analysis*

The XRD profiles of CaO and KF/CaO catalyst are presented in Fig. 2 as A&B. From the figure, it was signified that $KCaF_3$ was produced through the calcinations route of KF/CaO. Lime, calcite and portlandite were present in CaO XRD spectra. Various phases for instance portlandite, calcite, lime, $KCaF_3$ are shown in the KF/CaO XRD spectra. The 2θ angle (°) of the phases was 18.02, 34.08 of

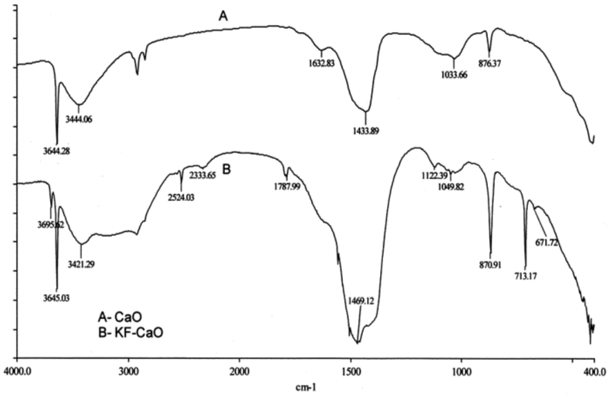

Fig. 1 — (a) FTIR spectra of CaO, and (b) KF/CaO.

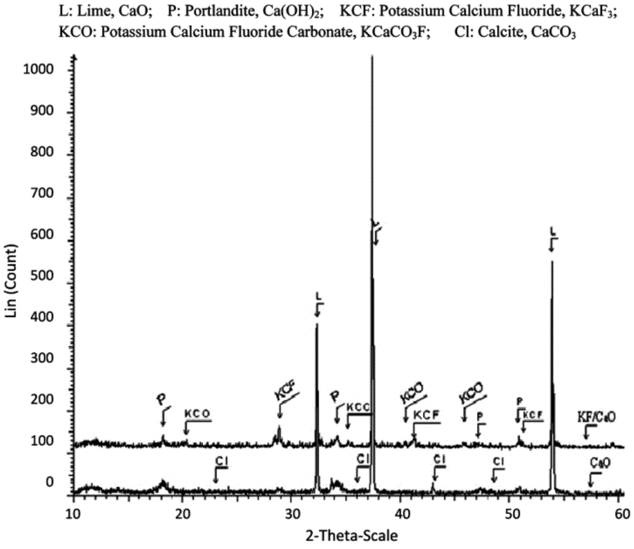

Fig. 2 — XRD spectra of CaO and KF/CaO catalyst.

$Ca(OH)_2$, 28.74, 41.22, 51 of $KCaF_3$, 32.1, 37.2, 54 of CaO observed in the KF/CaO. The peaks of $Ca(OH)_2$ and $KCaCO_3F$ almost disappeared at the calcination temperature of 600°C. The narrow peaks observed in the XRD spectra indicate the presence of large crystallites on the surface of the support[15]. From the XRD pattern of the catalyst, the KF peak appears as $KCaF_3$. It suggests that the active compound of KF got interacted with support material and forms the $KCaF_3$ active catalytic phase. Such observation in the literature was also observed by Hu *et al.* in a separate work on biodiesel production from Stillingia oil[16]. Adding KF to CaO results in $KCaF_3$ formation, which improves catalytic activity and catalyst stability. Because electronegativity of $F^-$ is greater as compared to oxygen, $Ca^{2+}$ in $KCaF_3$is a strong Lewis acid with a stronger $CH_3O^-$fascination. At the same time, $F^-$ is a robust base with more attractiveness for $H^+$. It makes $KCaF_3$ easier to convert CH3OH to CH3O−. Hence, the gathering of more $CH_3O^-$ ion on the KF/CaO catalyst's surface that easily attacks the carbonyl carbon of triglyceride of Jatropha oil has lead to increase the efficiency of transesterification. Furthermore, $KCaF_3$ 's function in KF/CaO is to increase the mechanical and structural strength of the catalyst that holds the microstructure in the chemical reaction and enhances catalyst's catalytic activity in biodiesel synthesis[17]. Thus, the catalytic activity in KF/CaO having $KCaF_3$ was greater than CaO for the transesterification reaction.

### *3.1.4 $CO_2$-TPD*

CaO and KF/CaO $CO_2$-TPD is presented in Figs 3 and 4 respectively. $CO_2$-TPD was mainly studied to interpret the basicity of the catalyst. The temperature of the $CO_2$ peak area, peak appearance, and the peak height were used to calculate the basicity of the catalyst. From the figure, it has been seen that 4 numbers of desorption peaks appeared at various temperatures in KF/CaO catalyst whereas three number of desorption peaks showed in CaO support. Results of $CO_2$-TPD of calcined catalyst and support are composed in Table 1. Silva *et al.* described that the feeble basic sites of catalysts are recognized at low temperatures and sturdy basic sites are referred to as high temperatures[18]. The first 2 peaks seemed at 282.6°C and 300.7°C, that are the feeble basic sites of the KF/CaO. Also, $CO_2$ interaction and the medium basic site present in the KF/CaO was desorpted at 400.2°C. A peak has occurred at 617.7°C because of the $CO_2$ interaction of the robust basic site with KF/CaO[19,20]. Nevertheless, with respect to CaO support, the low as well as moderate basic site of the catalyst recorded 2 desorption peaks at 339.3°C and 421.9°C.Further, a peak was recorded at 568.8°C for $Ca^{2+}$-$O^{2-}$ pairs of high basic strength[21]. CaO (201.64 mol/g) had a larger amount of basicity as compared to KF/CaO catalyst (117.17 mol/g). On the other hand, KF/CaO has shown better catalytic activity than the

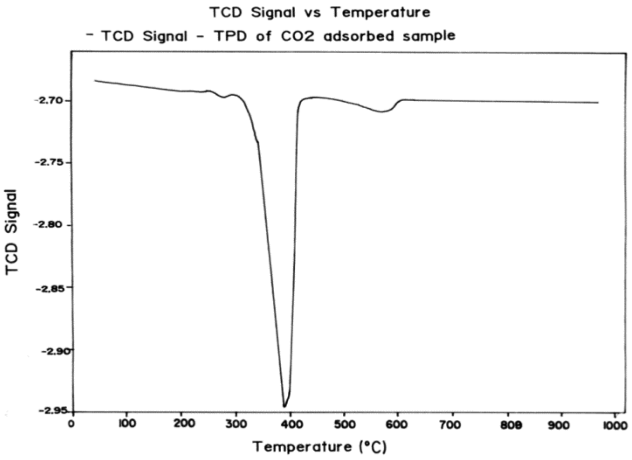

Fig. 3 — $CO_2$–TPD of CaO.

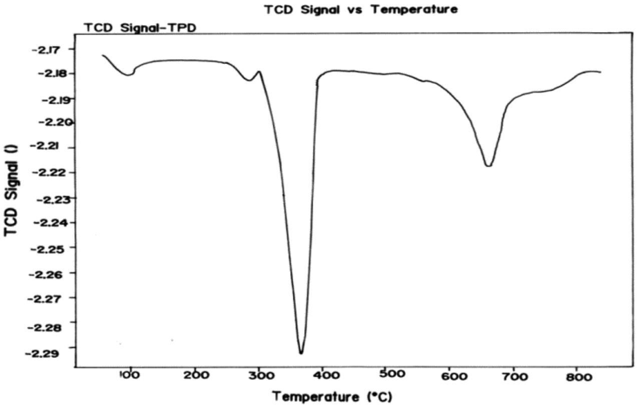

Fig. 4 — $CO_2$-TPD of KF/CaO catalyst.

Table 1 — Results of $CO_2$-TPD of calcined catalyst and support

| Sample | Temperature at maximum (°C) | Basicity (μmol/g) | $CO_2$-TPD |
|---|---|---|---|
| KF/CaO catalyst | | | |
| First peak | 282.6 | 25.88 | Weak basic site |
| Second peak | 300.7 | 17.88 | Weak basic site |
| Third peak | 400.2 | 70.91 | Medium basic site |
| Four peak | 617.7 | 2.50 | Strong basic site |
| CaO support | | | |
| First peak | 339.3 | 15.95 | Weak basic site |
| Second peak | 421.9 | 88.21 | Medium basic site |
| Third peak | 568.8 | 97.48 | Strong basic site |

CaO. Further, the CaO activity was declined because of poor SA. This could be due to the diffusion regulation among the reactant and the basic active sites within the pores of the catalyst. The justification was based on the study by Taufiq-Yap *et al*., on CaO-MgO mixed catalyst[21]. It was reported that least ratio of Ca/Mg (0.5) associated less basic site (429.2 µmol/g)but improved SA (15.1 $m^2$/g), whereas more ratio prepared catalyst with Ca/Mg (8) had shown least SA (4.8 $m^2$/g) with enhanced basicity (1210.5 µmol/g). In the catalytic activity, Ca/Mg (0.5) has shown high transesterification (90%) as compared to Ca/Mg (8). Therefore, SA played a significant role as compared to the basic site for transesterification. The surface of active sites of KF/CaO catalyst might be formed an interaction with methanol proton, which facilitated the methoxide ion formation for beginning the transesterification reaction. Hence, the active sites of the KF/CaO catalyst are more important towards the reaction of transesterification of the Jatropha oil.

#### *3.1.5 SEM Analysis*

The SEM images of CaO, KF/CaO at 600°C are shown in Figs 5 and 6 respectively. The SEM photograph of the CaO sample demonstrated that it was in the form of agglomerates which consist of very large particles. The shape of CaO was irregular and granules were sintered. The CaO sample has a particle size of 1–5 µm. When KF was loaded on CaO, the morphology was completely changed from the parent CaO. A porous structure is observed in Fig. 6. The KF/CaO catalyst was granular with 1–10 µm in diameter. A large number of particles combined to form aggregates. This kind of aggregates has been observed on the catalyst surface. It shows that the porous structure favors the access of Jatropha oil and methanol, which enhance the interaction between reactants and catalyst. These increased the catalytic capability and the efficiency of the transesterification reaction.

#### *3.1.6 EDX Analysis*

The EDX spectra of KF/CaO calcined at 600°C is illustrated in Fig. 7. According to the EDX image of the KF/CaO catalyst, the elemental alignment of K, F, Ca, and O on the catalyst surface is showed in the selected area 1. The elemental composition of the supported catalyst was determined by EDX and displayed in Table 2. EDX study indorses the amalgamation of active component KF on the surface of CaO.

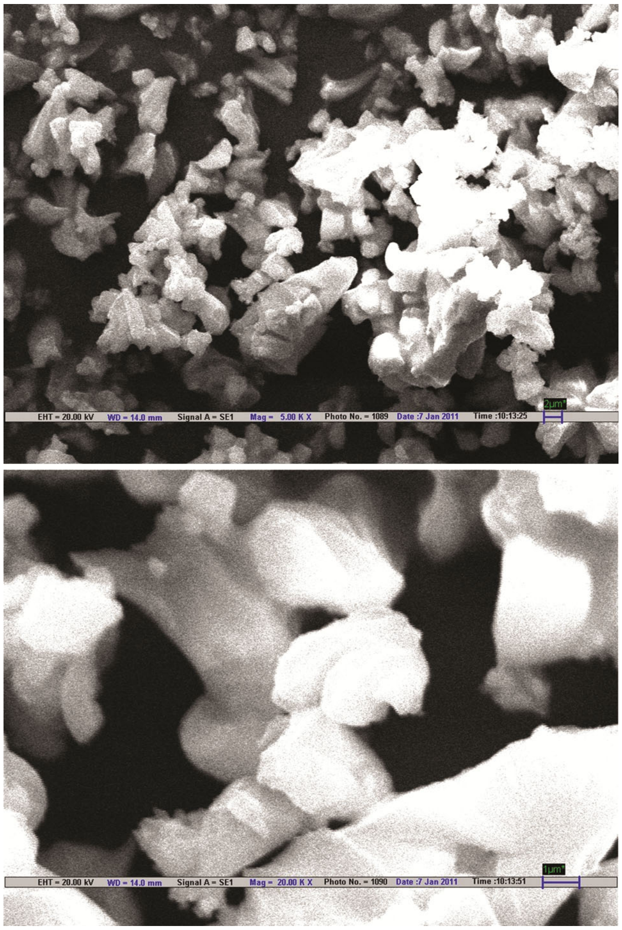

Fig. 5 — Scanning electron micrographs (SEM) of the CaO calcined at 600°C.

#### *3.1.7 TGA Analysis*

The TGA study of the KF/CaO is presented in Fig. 8. The TGA results illustrated that there was a slight weight loss between 50–180°C, which was the loosely physiosorbed surface water removal. The reduction in weight between 300–600°C indicates that the high-temperature calcinations supports the interaction between the CaO and KF to form KCaF3 new crystal active sites. The XRD data indicated crystalline structure formation during calcination.

#### *3.1.8 Particle Size Analysis*

The particle size distribution of KF/CaO and CaO catalyst were presented in Table 3. In case of KF/CaO, most of the catalyst particles, which are 90% below 104.88 µm and 10% below 4.35 µm, are observed. After the reaction of transesterification, most particles have large sizes; isolating the catalyst component from the reaction mixture is very simple. In view of all of the results of the catalyst characterization, we may assume that the $KCaF_3$ and

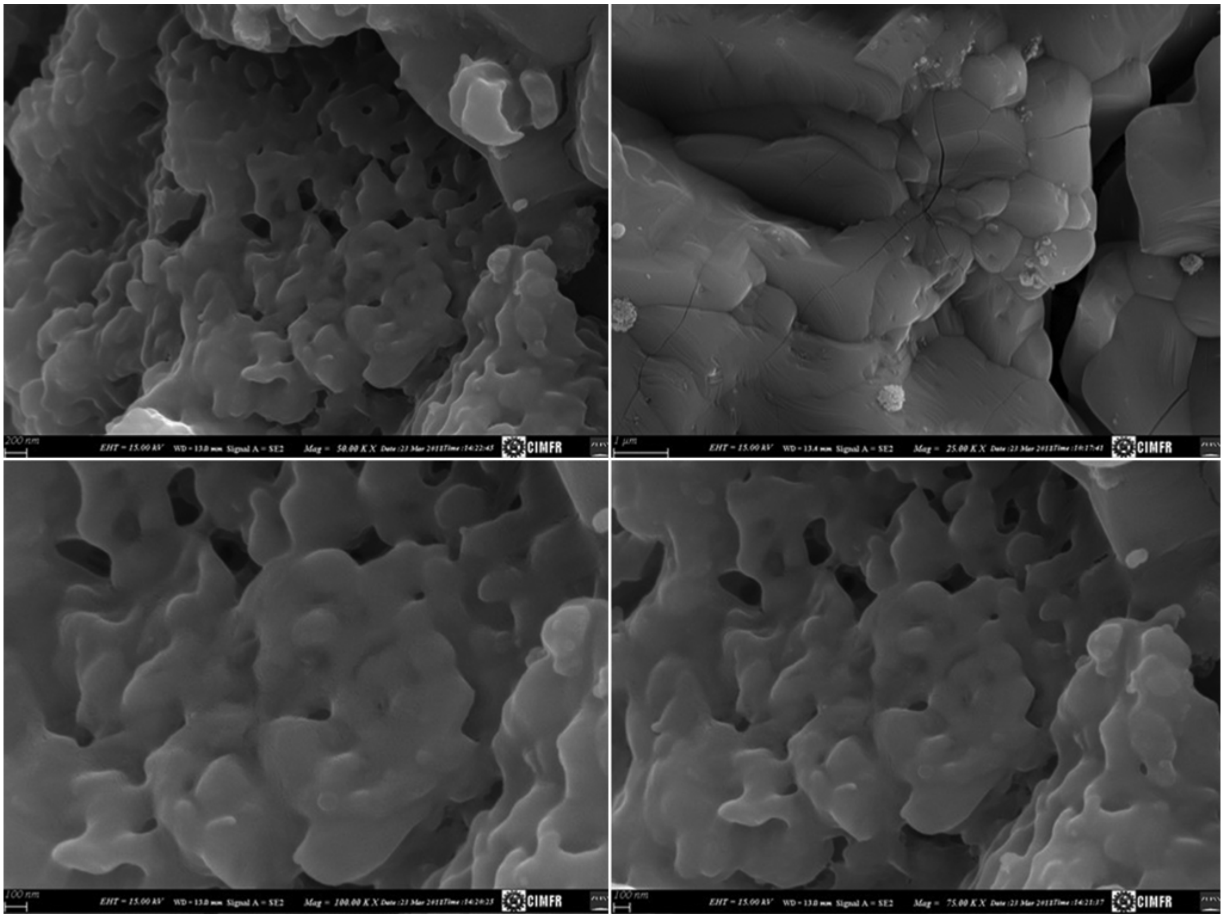

Fig. 6 — Scanning electron micrographs (SEM) of the KF/CaO calcined at 600°C.

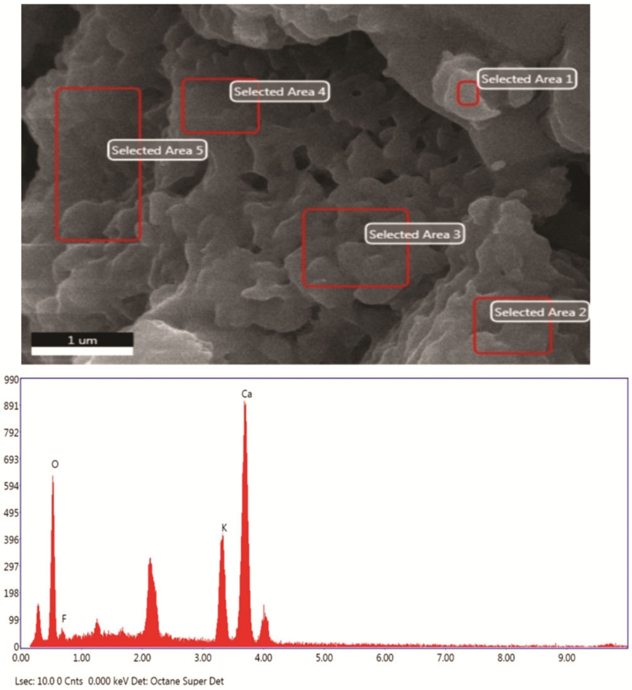

Fig. 7 — EDX spectra of KF/CaO calcined at 600°C

Table 2 — EDX analysis of KF/CaO catalysts at 600°C

| Element | Weight (%) | Atomic (%) |
|---|---|---|
| $O_K$ | 47.9 | 68.5 |
| $F_K$ | 2.6 | 3.1 |
| $K_K$ | 6.2 | 3.6 |
| $Ca_K$ | 43.3 | 24.7 |
| Total | 100 | |

Table 3 — Particle size distribution of CaO and KF/CaO Catalyst

| Sl. No. | Catalyst/support | <10% $d_{10}$ (µm) | <50% $d_{50}$ (µm) | <90% $d_{90}$ (µm) |
|---|---|---|---|---|
| 1 | KF/CaO | 4.35 | 26.97 | 104.88 |
| 2 | CaO | 6.65 | 25.18 | 80.26 |

the OH isolated group are the main active sites of the transesterification reaction.

### 3.2 Effect of Catalyst Reuse on Conversion

From CaO as supporting material, $Ca^{2+}$ was very prone for leaching in protonated solvents such as alcohol and water[22]. This $Ca^{2+}$ forms soap, which hinders catalytic activity and further influence the quality of the product. Further, CaO as catalyst acts as a homogeneous one (mineral acids), which hardly is reused. Thus stability study of this catalyst was conducted and the plot of catalyst reusability during biodiesel production is presented in Fig. 9. After each cycle, the used catalyst was filtrated, washed and dried followed by calcination at 600°C for 4 h to extract the organic deposits on the catalyst surface. It has been noticed that the amount of methyl ester is more than 90% even after the completion of the forth recycle. A gradual reduction in conversion efficiency has been observed with reuse of the catalyst. A 97% conversion efficiency at 1st use reduced to 93% by 4th reuse cycle. This must have happened due to slightly decay of catalysts, which attributed to leaching of active sites into the reaction mixture. Similar trend has been observed by Nisar *et al.*[23]. As a result of its long stability, thus, the KF/CaO catalyst can reduce the production cost of biodiesel. The decrease in conversion after forth recycling may be due to leaching property of KF in the KF/CaO catalyst.

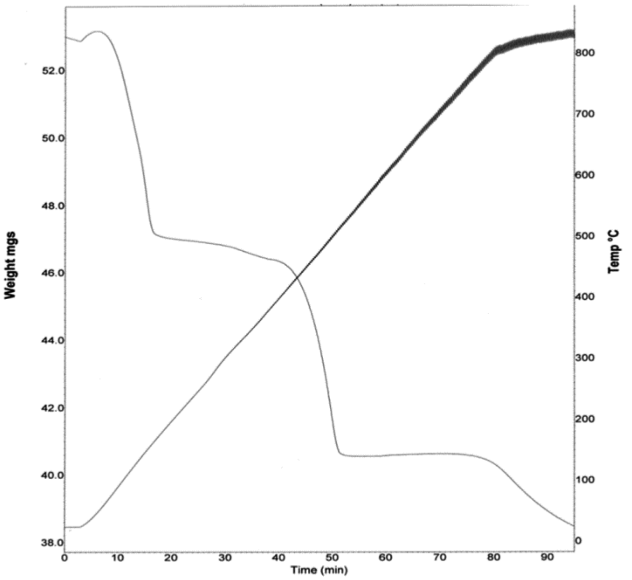

Fig. 8 — TGA graph of KF/CaO

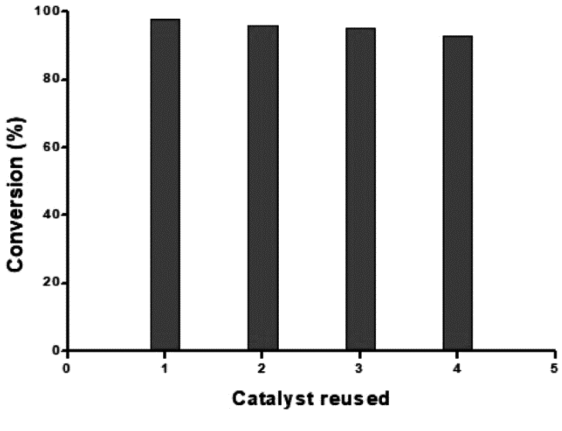

Fig. 9 — Catalyst reusability test

## 4 Conclusions

The basic target of this study was to inspect the KF/CaO catalyst characterization towards biodiesel production. A number of factors responsible for exceptionally enhancing the catalytic activity such as (1) free –OH group (ῡ 3645 $\text{cm}^{-1}$) and surface –OH group (ῡ 3695 $\text{cm}^{-1}$), these basic sites were facilitated the transesterification. (2) The strength of basic sites was evaluated through $CO_2$-TPD analysis as follows; weak basic sites at 282.6°C and 300.7°C, medium at 400.2°C and strong at 617.7°C, these basic sites were played the key role for enhancing the transesterification. The formation of $KCaF_3$ in catalyst preparation step was a major factor for increasing the catalyst efficiency due to the generation of Lewis acidic sites along with the basic sites. Mechanical strength and microporous structure of KF/CaO due to $KCaF_3$ was beneficial for better catalyst-substrate interaction and product formation.

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