Valorization of Restaurant Waste Oil Over Cow-bone Doped Siliceous Termite Hills Catalysts Towards Biodiesel Production

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Valorization of restaurant waste oil over cow-bone doped siliceous termite hills catalysts towards biodiesel production

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Abstract

Treated termite hill is a potent heterogeneous catalyst in the synthesis of biodiesel from restaurant waste oil (RWO). Two catalysts (raw cow-bone supported on silica; R-$SC_{1.5}$ and calcined cow bone supported on silica; K-$SC_{1.5}$) were developed and used in biodiesel production. The maximum conversion of RWO was 95.12 % using K-$SC_{1.5}$ at reaction time 2.5 h, methanol to oil ratio 9:1, temperature 65°C and catalyst loading of 2 %w/w. The prepared catalysts were characterized using SEM, EDAX, FTIR, XRD and BET analysis. The kinetics of the RWO with R-$SC_{1.5}$ and K-$SC_{1.5}$ was further studied. The E_a and A were found to be 41.4 kJ mol^{-1}, 53.41 kJ mol^{-1} and 2.24 $\times 10^4$ min^{-1}, 2.29$\times 10^6$ min^{-1} respectively. The transesterification reaction adhered to first order law, while physicochemical properties were within ASTM limits. Reusability of K-$SC_{1.5}$ was also examined, which revealed effectiveness up to 5 reuses without significant reduction in biodiesel yield.

Keywords: Biodiesel; Heterogeneous catalyst; Kinetic studies; Restaurant waste oil; Termite hill.

1. Introduction

In the world today, conventional fuels such as natural gas, coal, petroleum etc. are the major sources of energy, however their extensive use has an irreversible impact on the ecosystem through environmental pollution and global warming (Fadhila et al. 2017). Also, these fuels are non-renewable, and at the current rate of use, the tapped reserves are expected to decline critically within 50 years (Babatubde et al. 2020a). These problems prompted the search for substitute fuels which can be sustainably produced and consumed, with the added target of reduced toxic emissions upon combustion that may aid in reversing the climactic damage. These 'biofuels', so termed because of their origin from biomass based sources such as plants, animal or algae, have been accumulating research interest for the past few decades. Combined with other renewable sources such as wind, geothermal, hydroelectric, solar etc. the combined energy potential of these largely unused sources is far greater than can be from non-renewable energy sources, with ease of purification and use as well as energy density being the reasons for the latter's popularity. Biodiesel, being a form of biofuel, is gaining usage in engines and for power generation, yet widespread usage at this point is still largely impractical due to the scattered nature of potential resources. Biodiesel can be synthesized from renewable feedstocks, mainly edible or non-edible vegetable oils. Algae, animal fats, lard, and used oils from restaurants and households are also used as a cost-effective biodiesel feedstock (Dawodu et al. 2014). Polar alcohols (methanol, ethanol) are commonly used in a process known as 'transesterification' which involves conversion of glycerides or FFAs (free fatty acids) present in the feedstock into esters; however, recent studies by many researchers have shown that less polar alcohols such as 2-propanol are more effective in these conversions (Karmakar et al. 2021; Tan et al. 2010). Transesterification is also frequently coupled with esterification, usually as a pre-treatment step for oils that have high amounts of FFAs and are hence unsuitable for alkali-catalyzed conversion due to saponification and hydrolysis (Karmakar and Halder 2019). Here, polar alcohols could convert the FFAs into esters, usually aided by mineral acids that act as a catalyst, and non-polar alcohols are unable to participate in this conversion (Karmakar et al. 2020c). The benefits of biodiesel include biodegradability, high lubricity, low toxicity, high calorific value and high combustion efficacy due to increased oxygen (10 to 11%) and virtually no sulphur. Nevertheless, biodiesel commercialization is hindered by its high total cost of synthesis (Babatunde et al. 2020a). For catalyzed conversions, the prime factor that adds into production costs is catalyst

preparation cost and recovery or washing, since homogenous catalysts provide high ‘one-time; conversions but need to be washed away, typically over multiple rounds, while heterogeneous catalysts face issues of leaching and structural damage hindering their reusability apart from being costly to produce (Karmakar et al. 2018; Karmakar et al. 2020a). Additionally, feedstock procurement and processing (extraction, purification) amount for up to 30% of the total production costs, hence waste oils are a lucrative alternative (Dhawane et. al. 2018; Olutoye and Hammed, 2013). Therefore, there is a need to use low-cost feedstock such as restaurant waste oil (RWO) to reduce the total cost of biodiesel production and also solve the problem of fuel versus food competition (Jung et al. 2018). The Energy Information Administration estimated near 1 million gallon of RWO being generated per annum in USA alone. Also, in the EU countries, total RWO production was estimated to be 700,000 - 1,000,000 tons/year (Chhetri et al. 2008). Reports on RWO by several researchers have proven that it is a capable feedstock for biodiesel synthesis (Dhawane et al. 2018; Xiang-nan et al. 2019). Owolabi et al. and Rachael et al. established the efficiency of collected RWO as feedstock for biodiesel synthesis (Owolabi et al. 2011; Rachel et al. 2012). Kinetics of RWO transesterification needs to be elucidated for a better insight into its potential for scale-up (Ma et al. 2017). Most kinetic studies on RWO have been performed on processes that use homogeneous acids or bases as catalysts (Dhawane et al. 2018; Jain et al. 2011), however, process kinetics have not been studied by most researchers reporting their works on heterogeneous catalyzed conversions using novel synthetic catalysts.

Birla et al. reported the kinetic study of the transesterification of biodiesel from waste cooking oil using snail shell as catalyst (Birla et al. 2012). They found E_a of 79 kJ/mol and A of 2.98×10^{14} min^{-1}. Yusuf et al. reported transesterification kinetics of WCO conversion to biodiesel using anthill-eggshell-Ni-Co mixed oxide catalyst (Yusuf et al. 2017). The E_a and A were found to be 23.99 kJ/mol and 1.62×10^{6} min^{-1} respectively. Comparing this result with Birla et al., it could be stated that the anthill-eggshell-Ni-co mixed oxide catalyst is faster due to lower E_a and A, emphasizing the impact of catalyst nature on process kinetics (Birla et al. 2012; Moradi et al. 2015). According to Zhang et al., one way to reduce biodiesel synthesis cost is the full utilization of municipal or agricultural waste resources like cow bone (Ayoola et al. 2018), eggshell (Zabeti et al. 2009), snail shell (Birla et al. 2012; Laskar et al. 2018) as catalysts since they are rich in calcium and when properly activated (Zhang et al. 2010), are very stable with high surface area and porosity, resulting in enhanced catalytic performance. Among the calcium-rich waste

materials, cow bone has been selected as the heterogeneous base catalyst as it is abundant in nature, readily available and inexpensive (Birla et al. 2012). Furthermore, the efficiency of this heterogeneous base catalyst could be improved if properly supported on suitable materials.

Several heterogeneous base catalysts supports have been utilized ranging from base catalyst supported on carbon material or silica material or alumina material or zeolite material or clay material to metal oxides (Changmai et al. 2020; Hossain et al. 2019; Minh et al. 2019). Although, other supports have also shown to be effective, base catalysts supported on silica have gained more attention for biodiesel production because of its inertness in addition to possessing high surface area and structural stability (Polshettiwar et al. 2009; Samart et al. 2010). Moreover, Farook et al. has documented similar report stating that silica provides ample surface area for any metal to disperse (Ciriminna et al. 2013; Farook et al. 2006). Hence, silica has been widely selected as a support for the base catalyst used in the biodiesel production. Precursors such as rice husk ash (Farook et al. 2006), tetramethoxysilane (TMOS), tetraethoxysilane (TEOS), tetrapropoxysilane (TPOS) (Paulino and Schuchardt 2002), microcrystalline silicon oxide, silica sol, water glass (Shaikh et al. 1993) and termite hill (Ganguli et al. 2013) are excellent sources of silica. Most of these sources are difficult to obtain and/or process, however, termite hills are indigenous to Nigeria and because of this natural abundance as well as their chemical inertness and thermal stability, they have been chosen as a catalyst support of the base catalyst used in this work (Karmakar et al. 2020a). Moreover, termite hill has also been found to contain some oxides and silicates of calcium, iron, aluminium and potassium which are also important catalyst for biodiesel production (Ganguli et al. 2013). A few works such as by Enagbonma et al. and Kumar et al. have reported the use of termite hill as useful sources of bacteria for biofuel production; and except for our previous work (Karmakar et al. 2020a), sufficient literature on the suitability of termite hills as an inert, porous catalyst support for biodiesel synthesis does not exist (Enagbonma et al. 2019; Kumar et al. 2015).

For this study, a heterogeneous catalyst was produced using silica derived from termite hill to support CaO rich material. Transesterification of restaurant waste oil occurred in the presence of the prepared catalyst for synthesis of biodiesel. Process parameters such as time, catalyst amount, reaction temperature and methanol to oil ratio were selected as the operating parameters. Kinetic study was carried out. The reaction rate constant (k) and activation energy (E_a) at different

temperatures were elucidated. Fuel properties were also tested and equated with the American Standard for Testing Materials (ASTM).

2. Resources and procedure

2.1. Required materials

The restaurant waste oil (RWO) used as feedstock was obtained from the school restaurant, University of Ilorin, Kwara State, Nigeria. The RWO was preheated to eliminate moisture contents and later filtered to remove impurities. Termite hill abundantly available in the local area of Gidan Kwano, Minna, Nigeria, was selected as the precursor in preparing catalyst support (called silica). The cow-bone was obtained from Saraki abattoir in Ilorin. Methanol (98.9%) and H_2SO_4 (98.9%) were purchased from Sigma-Aldrich in Ilorin. Distilled water was obtained from the Chemical Engineering Laboratory, University of Ilorin.

2.2. Catalyst synthesis

To prepare the support, the termite hill was pulverized into powder. The powder was dissolved in distilled water and mixed thoroughly and left standing for 36 h. After decantation of the excess water, the termite hill was air-dried for 2 days, crushed into powder and dried again in an oven at 120 °C for 2 h to remove residual moisture. The powdered termite hill was sieved using 75 µm mesh and kept in a desiccator. Thereafter, powdered 100 g of termite hill was mixed with 200 mL aqueous solution of 1M NaOH under gentle agitation at 110 °C for 3 h (Putra et al. 2018). Resulting termite hill suspension was filtered and quenched by adding 300 mL ice-cold water, followed by filtration to obtain a silica type phase. Thereafter, it was repeatedly washed with hot distilled water to eliminate impurities as reported by Achyut et al., dried in the oven at 80 °C for 30 min and then labeled (S) (Achyut et al. 2010). In the same vein, collected cow-bone was washed, rinsed, dried, and ground into powder using a mechanical grinder, sieved and oven-dried at 110 °C for obtaining a stable weight (called C).

To prepare the catalysts, the pretreated cow-bone (C) 1.5 wt % (relative to the weight of support) was added to 10 g silica. The mixture was dissolved in 50 mL water before being placed in an orbital shaker at 200 rpm and kept at 30 °C overnight. Filtration of the solution yields a solid sample ($SC_{1.5}$), which was dried at room temperature for 24 h and called raw cow-bone

supported on silica (R - $SC_{1.5}$). The R - $SC_{1.5}$ was then calcined at 900 °C for 2 h, and then called calcined cow bone supported on silica (K- $SC_{1.5}$) and then stored in a desiccator.

2.3. Catalyst Characterization

The prepared catalysts (R - $SC_{1.5}$. and K - $SC_{1.5}$) were analyzed to estimate its physical properties such as surface area and pore volume. The analysis was performed using the multi-point BET (Brunauer Emmett Teller) method (Quantachrome instrument version 11.03, NOVA 2200E, Durham, USA**).** The catalysts were degassed at 196 °C under vacuum for 3 h, which preceded the physical adsorption measurements. The time of analysis was 72.8 min using N_2. A scanning electronic microscopy (SEM) [JEOL, JSM-6510LV, USA] was used to examine the surface morphological structure of the catalysts. The SEM displayed the image of the sample surface at a magnification of 100 µm on a mode of 15 kV average voltages and the elements present on the surface were quantified by using X-ray energy dispersive analysis (EDAX) using OXFORD Instrument INCAX-sight. The X-ray diffraction (XRD), EMPYREAN diffractometer system with CuKα radiation of (λ=1.54060 Å) at 45 kV, step size of 2θ 0.0260, scanning step time of 29.07 seconds and 40 mA between the range of 2θ = 15.0024 to 74.9684° was used to determine the chemical phase and the crystalline structure of the functionalized catalyst. The presence of the functional groups was confirmed by using Fourier transform infrared spectrophotometer (Shimadzu FTIR-8400S, Canada) displaying a wave number spectrum between the range of 500 cm^{-1} - 4000 cm^{-1}.

2.4. Conversion process

Catalyst performance was examined during transesterification, conducted using a magnetic stirrer hotplate and a 250 mL round bottom flask attached with a condenser and a thermostat to maintain a constant temperature during the reaction. Based on 50 g of RWO, with constant agitation rate of 250 rpm, the reaction took place under the operating conditions of 9:1 methanol to oil ratio, a reaction time of 2.5 h, catalyst loading of 2 wt % (for R- $SC_{1.5}$ and K- $SC_{1.5}$) and reaction temperatures of 50, 55, 60, and 65 °C. After the reactions, each mixture was poured into separating funnels through filter paper to retain the catalyst for reuse. The filtrate mixture was allowed to separate overnight to obtain a clear layer of biodiesel. The produced biodiesel was collected, purified (through repeated wet—washing and drying) and volumetric fuel yield was

calculated using Eq.1. To investigate the quality of the biodiesel synthesized, physico-chemical tests were performed as per ASTM standards.

$$Biodiesel\ Yield\ (\%) = \frac{Weight\ of\ Biodiesel\ from\ RWO}{Weight\ \ of\ RWO\ used}\ x\ 100\ \% \quad (1)$$

2.5. Kinetics of transesterification of RWO

For kinetic studies, considered assumptions were:

1. Methanol concentration is in excess of required stoichiometric ratio and can be considered constant. Thus, the reversible reaction could be ignored as equilibrium is shifted towards product formation (Le Chatelier's principle).
2. The catalyst efficiently catalyzed every step-wise conversion of the transesterification, and the three consecutive reactions cycles occurred at the same rate as the overall rate of triglyceride conversion (Yusuff et al. 2017),

Moreover, Karmakar et al. have also reported that excess methanol is required to avoid the conversion of glyceride while maintaining a forward reaction (Karmakar et al. 2020a). Therefore, the rate law governing the forward reaction of transesterification reaction has been expressed in Eq.2.

$$-R_a = \frac{-d[TGs]}{dt} = k'.[TG].[MtOH]^3. \quad (2)$$

Where $-R_a$ = rate of reaction; TG_s = triglyceride concentration, k' = equilibrium rate constant, MtOH = methanol concentration. Since, the concentration of methanol did not alter the reaction order, it is appropriate to theorize that the reaction adheres to a pseudo-first order reaction. Hence, the Eq.3 has been adapted for the reaction order.

$$-R_a = \frac{-d[TG]}{dt} = k.[TG]. \quad (3)$$

Where k is modified rate constant, and therefore $k = k'[MtOH]^3$. It has been assumed that at time t = 0, the initial concentration of triglycerides was TG_0 mol/dm^3, and at time t it falls down to TG_1. On integrating Eq.3 we have Eq.4, noting that $[TG] = [TG_o](1 - X)$

$$-\ln(1 - X) = kt. \quad (4)$$

The graph of *–ln(1 - X)* against *t* at different reaction temperatures (50 °C, 55 °C, 60 °C, and 65 °C) was plotted to obtain the rate constants at each temperature. Furthermore, to determine the

activation energy (E_a, kJ/mol) and the frequency factor (k_a, min^{-1}) of the reaction, the values of the rate constants obtained at different temperatures were plotted against the inverse of temperature.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. BET analysis

The BET analysis of both K - $SC_{1.5}$ and R - $SC_{1.5}$ were performed and presented in Table 1. The calcined cow bone supported on silica (K - $SC_{1.5}$) shows a wider surface area of 440.88 m^2 g^{-1} as compared to the raw cow bone supported on silica (R - $SC_{1.5}$) with surface area of 260.70 m^2 g^{-1}. This indicates that during the calcination process, the components of the catalyst which tend to hold the particles together have been burnt off thereby increasing the areas to be occupied by the active sites. Furthermore, Birla et al. reported that a higher pore size of a catalyst is necessary as it allows proper diffusion of reactants into the active site of the catalyst (Birla et al. 2012). In this work, the pore size of K - $SC_{1.5}$ (22.90 nm) was larger than R - $SC_{1.5}$ (21.24 nm), hence, this allowed sufficient interactions between the catalyst, reactants and product molecules. The concentration of basic site of the catalyst was also investigated and the value of the R - $SC_{1.5}$ (9.40 mmol/g cat) was found to be lesser than K - $SC_{1.5}$ (10.90 mmol/g cat), this result could be attributed to the oxides of calcium and other basic compounds as reported by Yusuff et al. Furthermore, it also indicates that Lewis base site contributed to high catalyst activity (Yusuff et al. 2017).

3.1.2. Morphological analysis

SEM studies in Fig. 1 shows the structural nature of the raw and calcined catalyst developed respectively. Fig. 1a revealed that the catalyst particles (X) of R - $SC_{1.5}$ are agglomerated and heterogeneous. It possesses coarse and irregularly sized particles with smooth edges. This result is congruent to reports from Mitaphonna et al. when they stated that catalyst particles formed with uncalcined cow bone could be coarse and possess aggregate structure with smaller surface area (Mitaphonna et al. 2019). However, Fig. 1b obviously reveals a deviation in particle size (Y) after calcination (Kusuma and Chandrappa 2019). The particles tend to be dispersed and reduced in size with higher surface area. This indicates that the organic compounds in the K-

$SC_{1.5}$ have undergone decomposition, while the inorganic compounds have been converted to their oxides (Ganguli et al. 2013; Mitaphonna et al. 2019). The irregular sized particles tend to have rough edges (Y) which is expected to enhance adequate interaction between the reactants. This result is also congruent to BET results from other studies (Babatunde et al. 2020a).

3.1.3. EDAX analysis

As shown in Fig. 2, the EDAX analysis reveals the elemental compositions of the R-$SC_{1.5}$ and K-$SC_{1.5}$ respectively. The presence of silicon (Si) aluminium (Al), iron (Fe), zinc (Zn) and titanium (Ti) in the two catalysts was due to the natural composition of termite hill (as explained by Ganguli et al.), while the calcium (Ca) was impregnated from cow bone (Ganguli et al. 2013; Nisar et al. 2017). The R - $SC_{1.5}$ contains 63.1 % Si, 17.9 % Ca and 5.1 % K while K-$SC_{1.5}$ has a higher percentage composition of 65.85 %, Si, 21.99 %, Ca and 6.9 % K. The results from the EDAX indicate that the calcination process had a notable effect on the catalyst composition (Farooq et al. 2015; Figueiredo et al. 2010)**.** However, the reverse is seen for aluminium (Al), iron (Fe), zinc (Zn), magnesium (Mg) and titanium (Ti) where their compositions were shown to be higher in R - $SC_{1.5}$ than K - $SC_{1.5}$. These elements may have also enhanced the catalytic performance of R - $SC_{1.5}$ during the transesterification reaction even without calcination. Lastly, a slight change was also noticed in the percentage composition of sodium (from 2.07 % to 1.73 %) and aluminium (from 0.13 % - 0.07 %) between the two catalysts. Also, Table 2 shows the chemical composition of the calcined cow bone as determined by XRF analysis. It reveals the presence of CaO (62.81%) and P_2O_5 (35.4%) and other compounds in lower quantity. The result implies that cow bone is a suitable source of catalyst for biodiesel production. The reported work by Nisar et al. shows good agreement with the findings reported in this study (Nisar et al. 2017). Moreover, the cow bone contains Fe_2O_3 (0.45 %), CuO (0.004 %), ZnO (0.015 %), SrO (0.161 %), CeO_2 (0.071 %), K_2O (0.25 %) and Li_2O (0.839 %) at very low percentages. Even at lower percentage, they could also have contributed to the catalyst reactivity. This further confirmed the results obtained from the EDAX analysis.

3.1.4. Spectral analysis

The X-ray diffraction analysis of the K-$SC_{1.5}$ was further investigated to determine the size and crystallinity of the synthesized material. As shown in Fig. 3, 2θ values from 15°-75° reveal the nature and crystallinity of the materials. The peaks at 32.49° and 53.62° indicates the presence of

SiO_2 (quartz) in the form of a rhombohedra crystal. The peaks at 34.12°, 47.11°, 63.97°, 68.11°, and 69.24° also indicate the presence of CaO in the form of the cubic crystal system (Farooq et al. 2015). Hence, the XRD analysis revealed the presence of two prominent crystalline phases derived from silicon oxide (SiO_2) and calcium oxide (CaO) (Lesbani et al. 2013). The traces of these compounds were also confirmed by elemental analysis. Presence of other compounds may be confirmed from other non-major peaks in the spectrum.

As depicted in Fig. 4, the FTIR spectrum of K-$SC_{1.5}$ was also investigated. The wavenumber between 3400 cm^{-1} and 3650 cm^{-1} represents symmetric and asymmetric -OH stretching of H-bonded water which could be as a result of moisture adsorption or the presence of $Ca(OH)_2$ in trace amounts (Varadwaj et al. 2013). The wavenumber 1600 cm^{-1} also revealed an H-O-H bending vibration of coordinated water molecules present in the interlayer structure. The wavenumbers 1428.39 cm^{-1} and 931.34 cm^{-1} can be correlated to stretching vibrations of CO_3^{-2} groups, in $CaCO_3$ (Lesbani et al. 2013). According to Varadwaj et al., the absorption band at wavenumber 578.14 cm^{-1} also suggested the presence of Ca-O as reported by (Varadwaj et al. 2013). Furthermore, the absorption spectrum at wavenumber 1096.11cm^{-1} suggested the presence of silicate ion (Si-O stretch) as a functional group in the material (Yusuff et al. 2017). The presence of all these stretches and vibration bonds may have been responsible for the high reactivity of the calcined catalyst (K-$SC_{1.5}$).

Furthermore, FTIR of the biodiesel produced using K - $SC_{1.5}$ at 65 °C under the stated conditions was examined. The spectrum in Fig. 5 shows the absorption band at wavenumber 3417.11 cm^{-1}, suggesting that the O-H stretching vibration may represent alcohols. The band of 1735.24 cm^{-1} suggests the vibration of double bonds stretching of ester carbonyl group of triglycerides (C=O stretch) which may be due to the presence of methyl esters. Other bands seen were at wave numbers 1450.5cm^{-1}, 1393.97cm^{-1}, and 749.23cm^{-1} which may also depict the presence of C-O ester groups (Yusuff et al. 2018).

3.2. Transesterification

Reactions were conducted in the presence of R-$SC_{1.5}$ and K-$SC_{1.5}$ under the operating conditions of 9:1 (methanol to RWO ratio), reaction time of 2.5 h, catalyst loading of 2 wt % relative to RWO and reaction temperatures of 50, 55, 60, and 65 °C (Adepoju et al. 2020; Nisar et al. 2017). The temperature was varied between 50-65°C so as to investigate the kinetics of the reaction. In

Fig. 6, the RWO conversion tends to increase as the reaction temperature increases. The maximum yields attained by R-$SC_{1.5}$ and K-$SC_{1.5}$ were 68.1% and 95.12% respectively. Hence, it is worthy of note to state that the higher conversion attained by K- $SC_{1.5}$ was due to the influence of calcination on the catalyst (Farooq et al. 2015).

3.3. Fuel properties

Physicochemical properties of the FAMEs obtained using K-$SC_{1.5}$ as catalyst was examined and compared with values set by the American Standard for Testing Materials (ASTM). The results are congruent with reports from Chinyere et al. as shown in Table 3, where the values were found to be within required range (Chinyere et al. 2017). High flash point and fire point specify transportation and fuel storage efficiency. Substantial improvement in calorific value was observed which implies that the fuel is energy efficient. Since increased fuel viscosity results inefficient atomization due to low lubricity, the low kinematic viscosity observed in the fuel is responsible for improved performance. The delay in a fuel's ignition can be measured by cetane number of the obtained product. The API gravity value obtained (39.61) also confirmed that the RWO-biodiesel is less dense relative to the density of water (Karmakar et al. 2020a).

3.4. RWO transesterification kinetics

The influence of temperature and time (using R-$SC_{1.5}$) on RWO conversion is revealed in Fig. 7a. Although the conversion of RWO remains low compared to K–$SC_{1.5}$, the R-$SC_{1.5}$ could show potential towards higher conversion of RWO in further studies. The influences of temperature and time (using K-$SC_{1.5}$) on RWO conversion is revealed in Fig. 7b. The effect of increasing the reaction temperature between 50 °C and 55 °C was obvious even as time increases from 30 min to 60 min. Also, the conversions curve tends to intersect each other between the reaction temperatures 55 °C – 60 °C. However, as time and temperature increase, the curves tend to split. This commensurate with reports from literature, as increase in temperature allows the mass transfer and proper dispersion of catalyst molecules.

3.4.1. Determining E_a and A

In order to deduce the kinetic parameters, -*ln*(1-x) was plotted against *t* as shown in Fig. 8 and the correlation coefficients were >0.9 for both catalysts. As shown in Fig. 9, the E_a and A were 41.4 kJ/mol and 2.24 $\times 10^4$ min^{-1} for R-$SC_{1.5}$ and 53.41 kJ/mol and 2.29$\times 10^6$ min^{-1} for K-$SC_{1.5}$

respectively. These were determined by plotting *ln*(k) of rate constants for each temperature against the inverse of reaction temperatures (1/T). In this plot, the R-squared values for R-$SC_{1.5}$ and K-SC_1 were found to be 0.9501 and 0.9959 respectively. The result was in agreement with reported works as the range of E_a observed in literature were mostly amid 33-84 kJ/mol (Deshmane and Adewuyi 2013; Feyzi and Shahbazi 2017). E_a values vary depending on process, feedstock and catalyst type (Endalew et al. 2011). Krishnamurthy et al. reported an E_a of 67.21 kJ/mol and A of $5.182\ x\ 10^8$ min^{-1} from the transesterification of scum oil (Krishnamurthy et al. 2020). Furthermore, Birla et al. documented activation energy of 79 KJ/mol and 2.98×10^{10} min^{-1} in converting waste cooking oil through a heterogeneous catalyst (Birla et al. 2012).

3.4.2. Reusability of K-$SC_{1.5}$

The reusability tests aimed at establishing the extent of leaching were carried out when the first cycle of transesterification reaction was completed. The test was conducted for 5 consecutive cycles under reaction conditions discussed earlier in this study. After completion of the reaction, filtration ensured recovery of the catalyst, and a subsequent wash using methanol. The conversion remains stable for the first three cycles and reaches 90.45 % at the end of the 5th cycle as shown in Fig. 10. The decrease in the yield of methyl ester is from the blockage of active catalytic sites in the support structure, along with loss of active metals from the catalyst due to leaching. This was in agreement with literature reports from Olutoye and Hameed, Adepoju et al. and by Karmakar et al. in their works with acid and base doped carbonaceous supports (Adepoju et al. 2020; Karmakar et al. 2020a; Karmakar et al. 2020b; Karmakar et al. 2020c; Karmakar et al. 2021; Olutoye and Hameed 2013).

4. Conclusion

In this study, we investigated biodiesel synthesis from restaurant waste oil (RWO) with R-$SC_{1.5}$ and K-$SC_{1.5}$ as heterogeneous catalysts. The K-$SC_{1.5}$ was found to give maximum biodiesel conversion of 95.12 % and fuel properties were found to be within ASTM limits. Also, based on maximum percentage conversion and information deduced from various characterizations such as SEM, FTIR, XRD, and EDAX, the kinetic studies of the restaurant waste oil was studied using K-$SC_{1.5}$. The E_a and A were found to be 53.41 kJ/mol and 2.29×10^6 min^{-1} respectively, which is congruent with most results reported in available literature. Hence, it could be stated that treated termite hill is a recommendable catalyst for the transesterification of RWO since it

reduces the total cost of biodiesel production and can also help promote the commercialization of biodiesel.

Ethics approval and consent to participate

Not applicable

Consent for publication

Not applicable

Availability of data and materials

All data generated or analyzed during this study are included in this article.

Competing interests

The authors declare that they have no competing interests.

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Authors' contributions

BEO conceptualized the study and listed necessary resources. **BK** and **BEO** handled software based experimental designing and formal analysis as well as data curation. They also wrote the original draft. **SHB**, **AFA** and **YA** were the experimental investigators who also validated obtained data, while **GH** was the supervisor and was in charge of this project. **BK**, **LR** and **GH** took the responsibility of reviewing and editing the manuscript. **GH** handled submission related procedures. The final version of the manuscript was read and approved by all authors.

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Figures

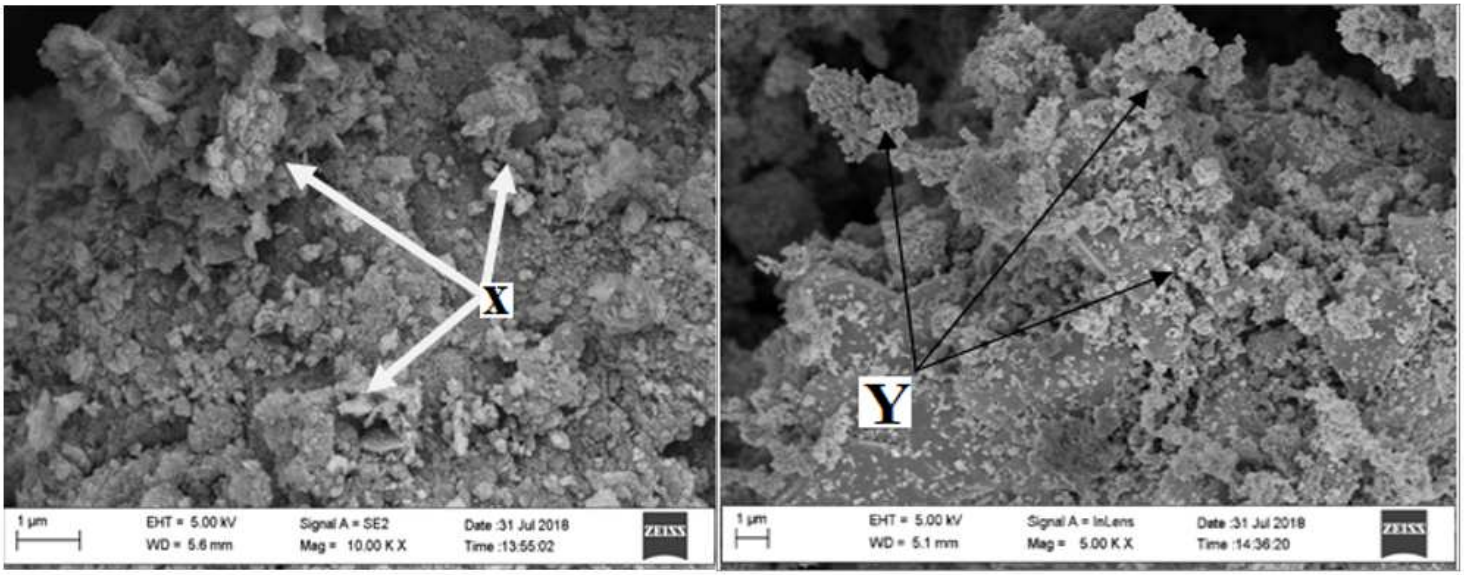

Figure 1

SEM Image of (a) R - SC1.5 and (b) K¬ - SC1.5

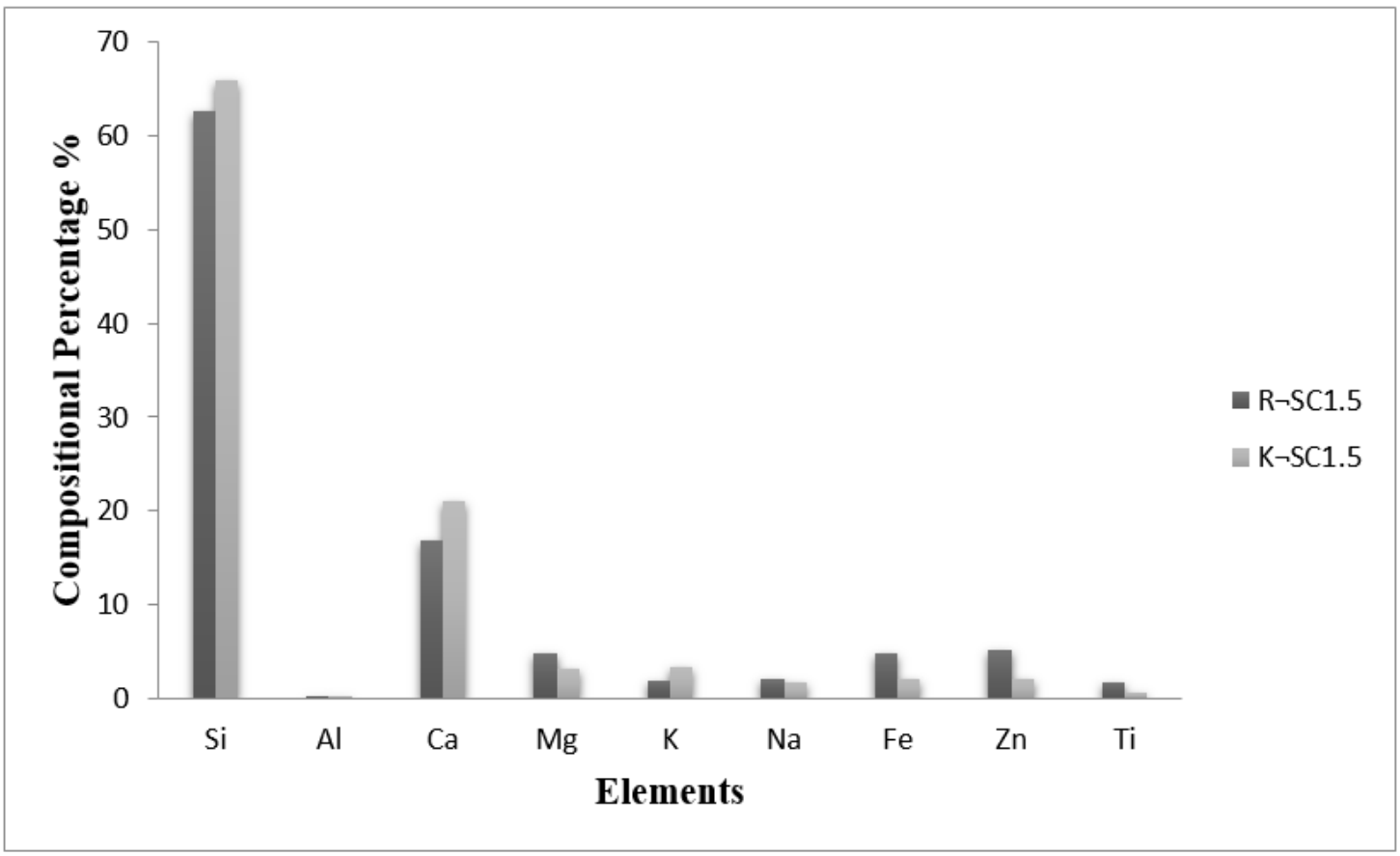

Figure 2

EDX analysis of the R - SC1.5 and K¬ - SC1.5

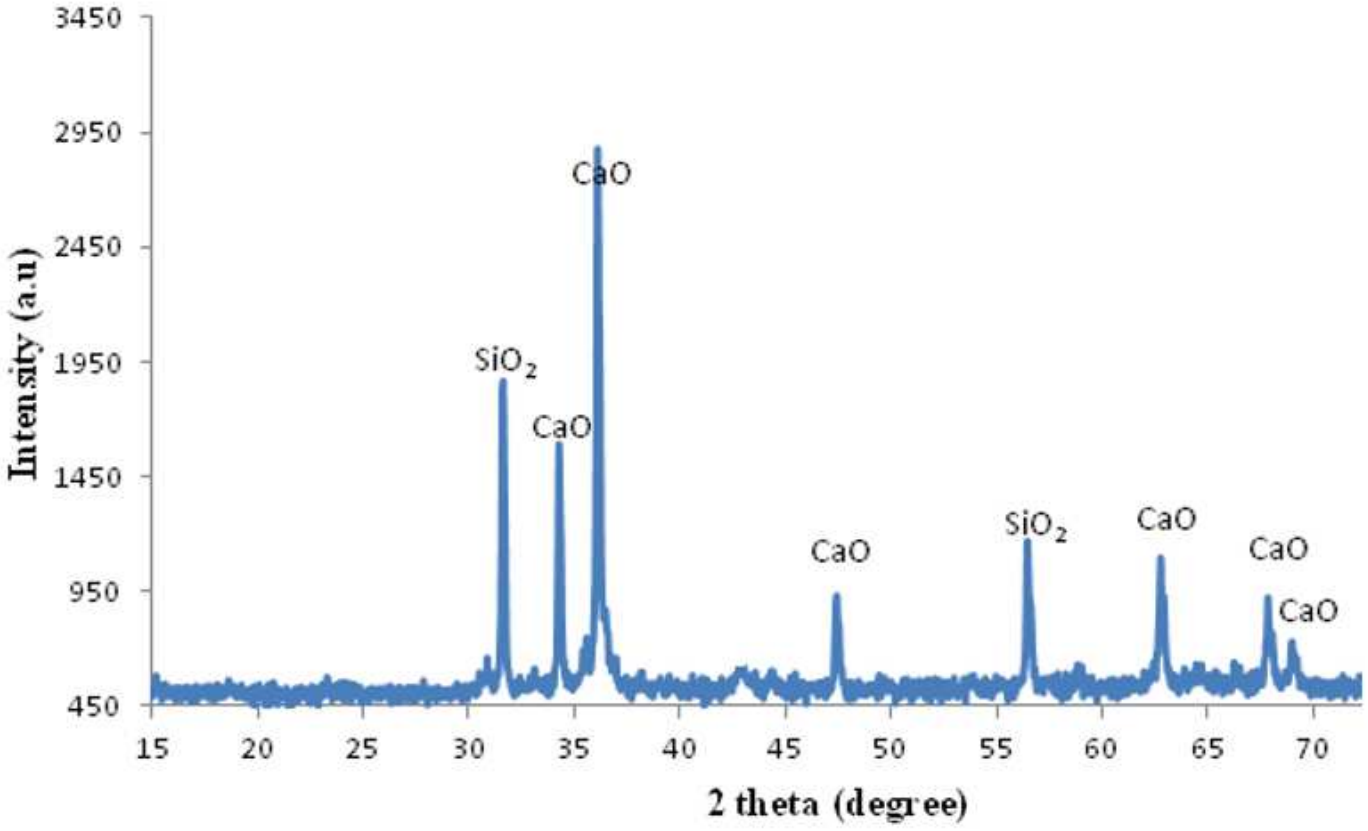

Figure 3

XRD Spectrum of K¬ - SC1.5

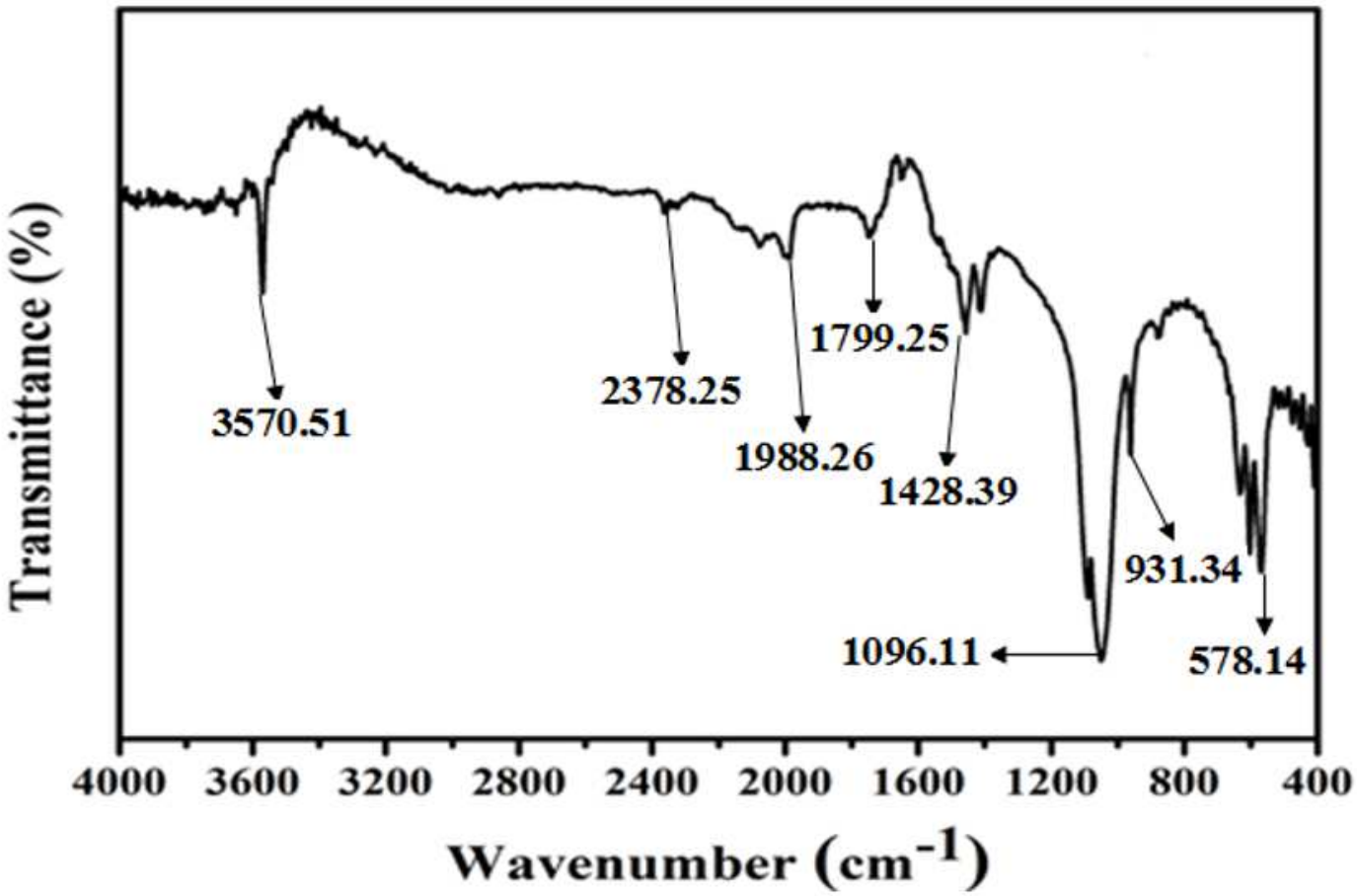

Figure 4

FTIR Spectrum of K¬ - SC1.5

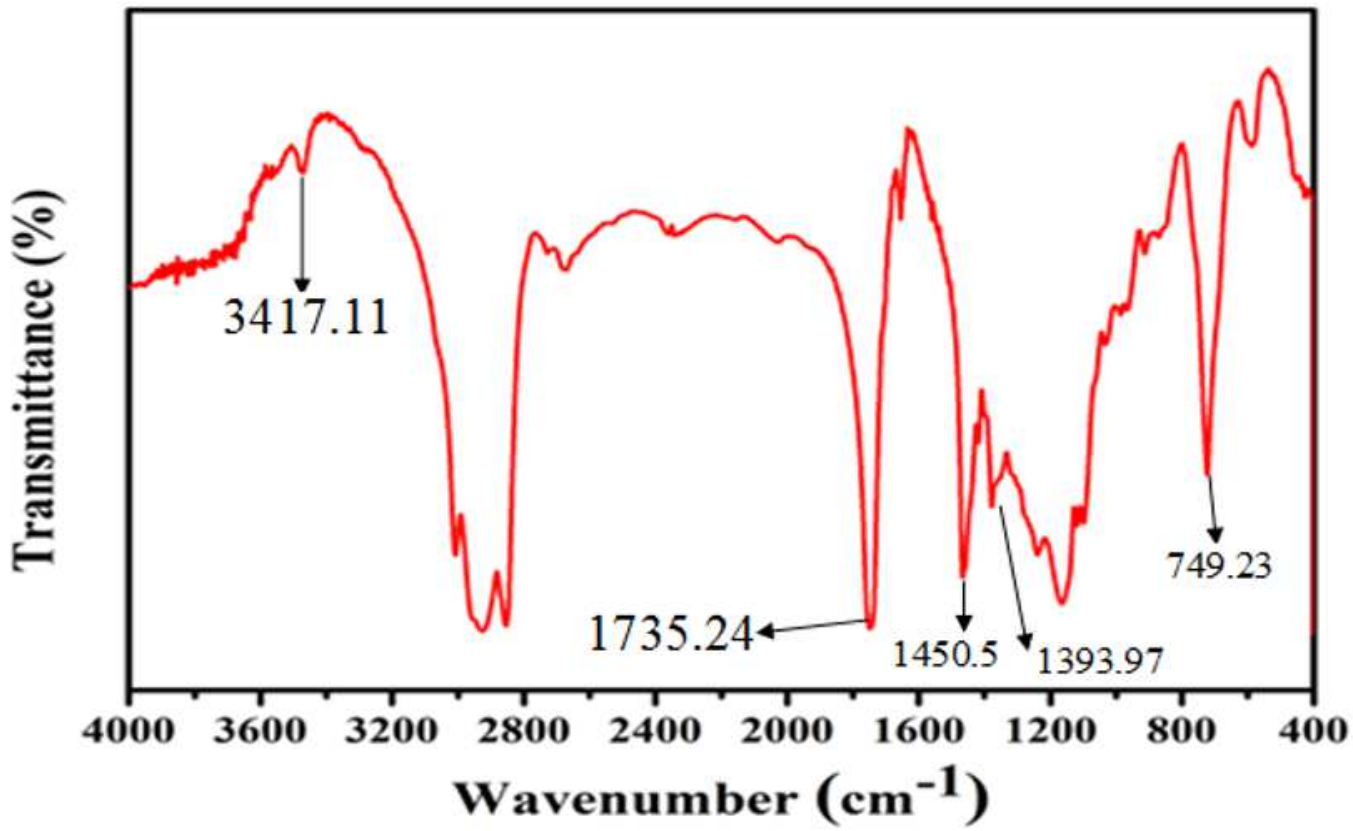

Figure 5

FTIR spectrum for biodiesel produced form K¬ - SC1.5 at 65°C after 2.5h

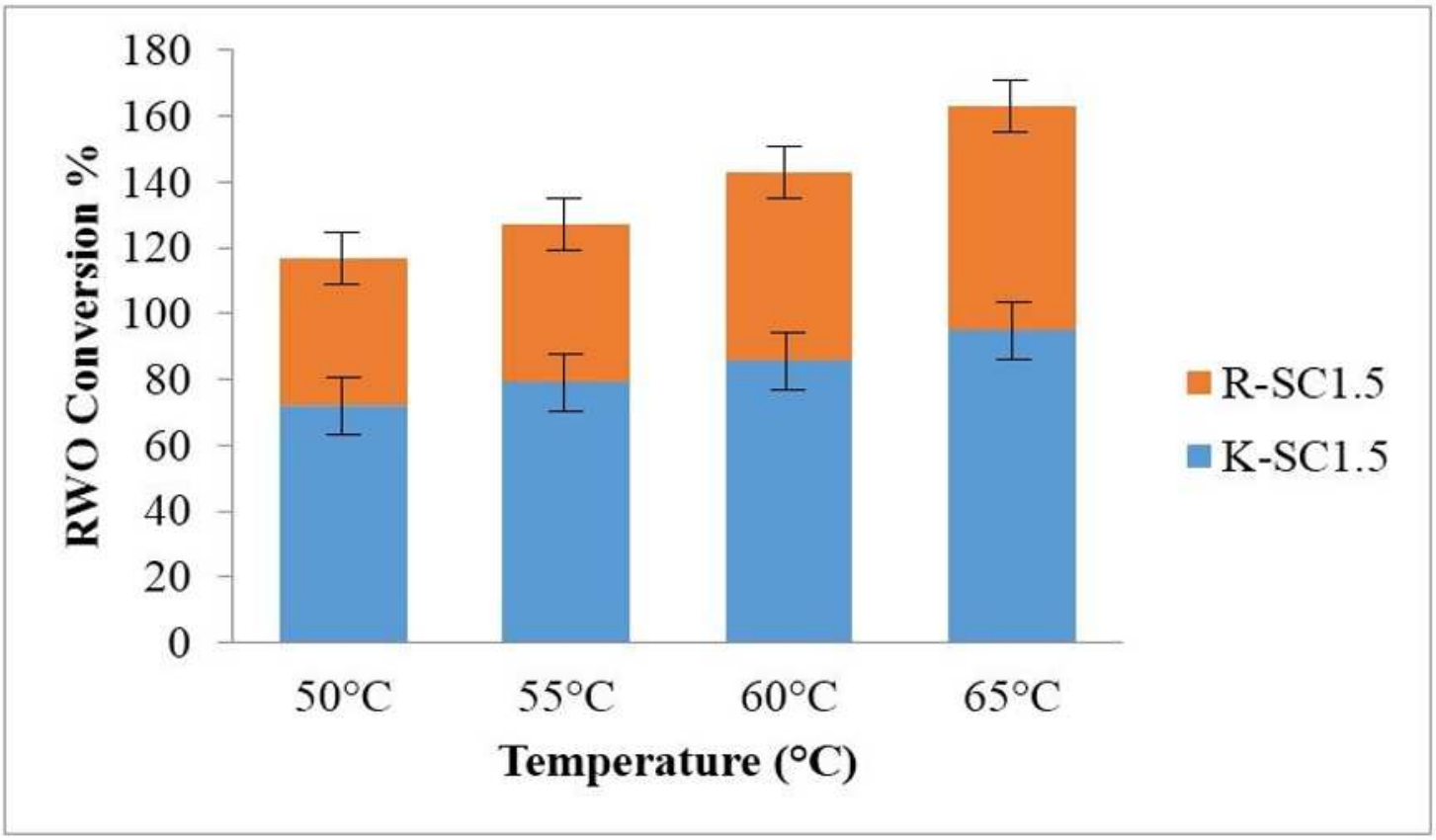

Figure 6

Maximum biodiesel conversion for R - SC1.5 and K¬ - SC1.5 after 2.5h

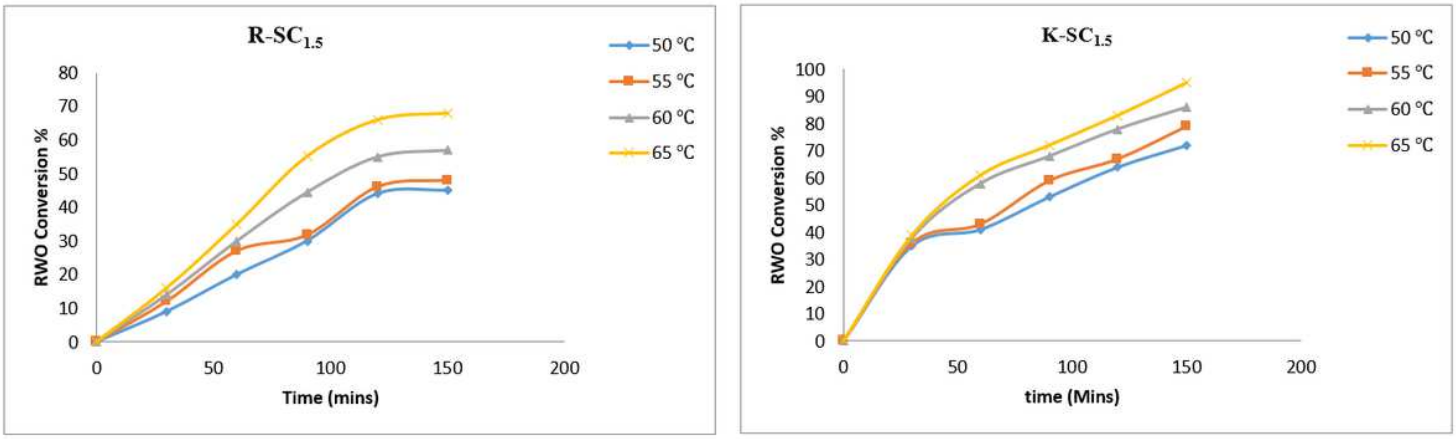

Figure 7

a Effect of temperature and time of RWO conversion (R-SC1.5) b Effect of temperature and time of RWO conversion (K-SC1.5)

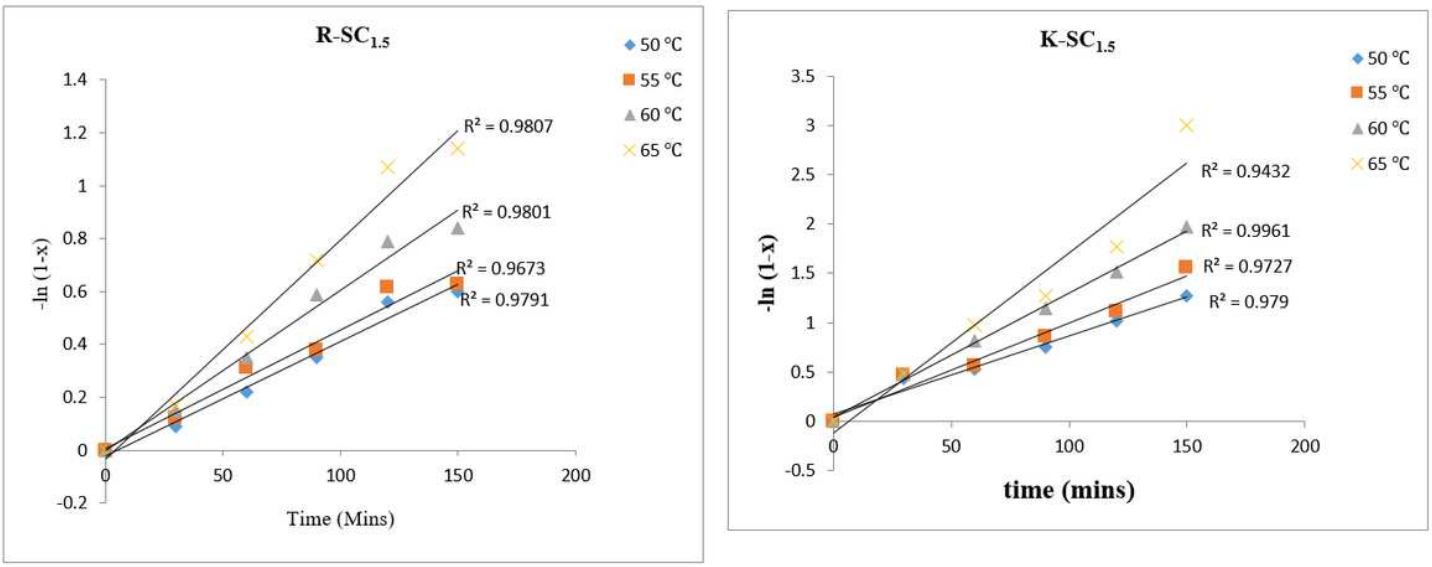

Figure 8

plot of - ln(1-X) against t

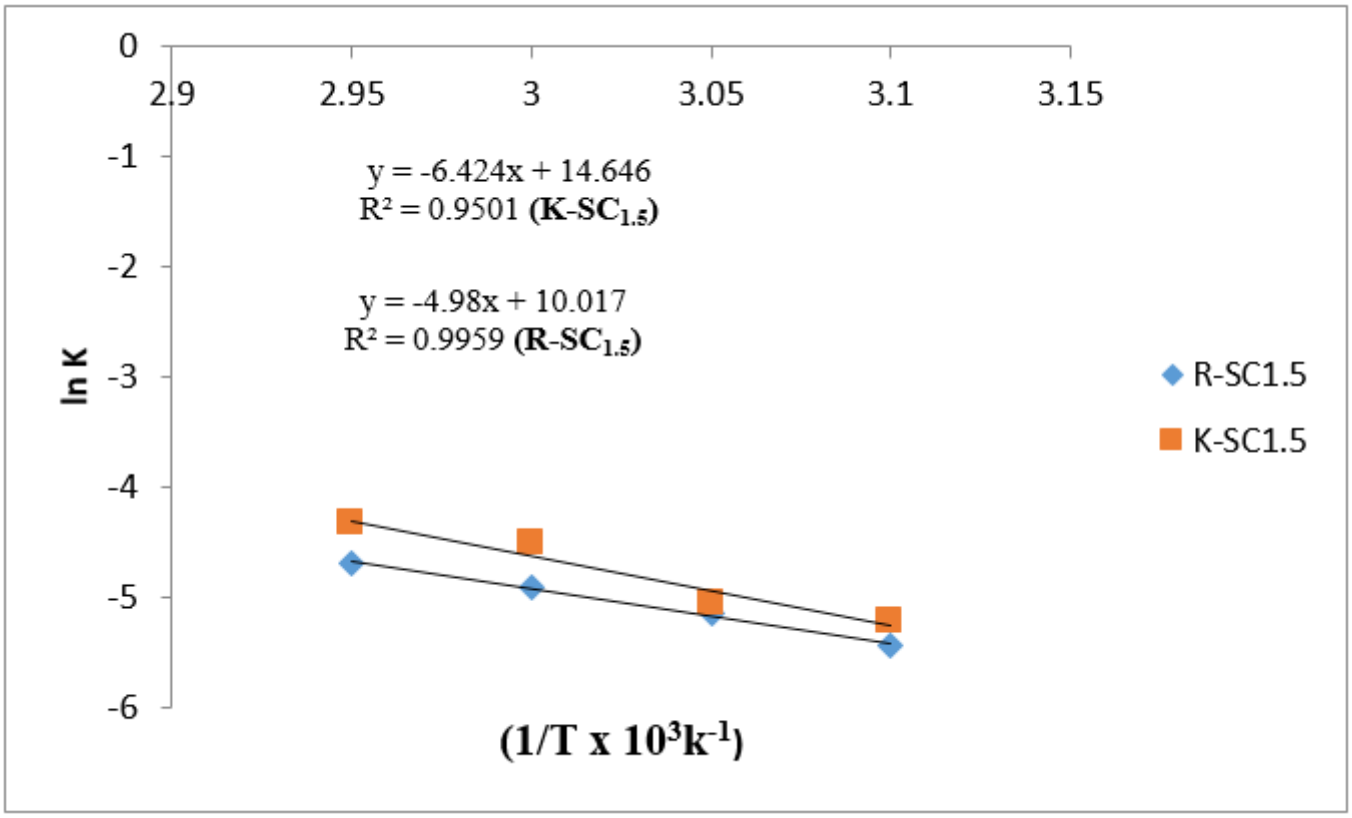

Figure 9

Plot of ln K against 1/T x 10-3 (R-SC1.5 and K-SC1.5)

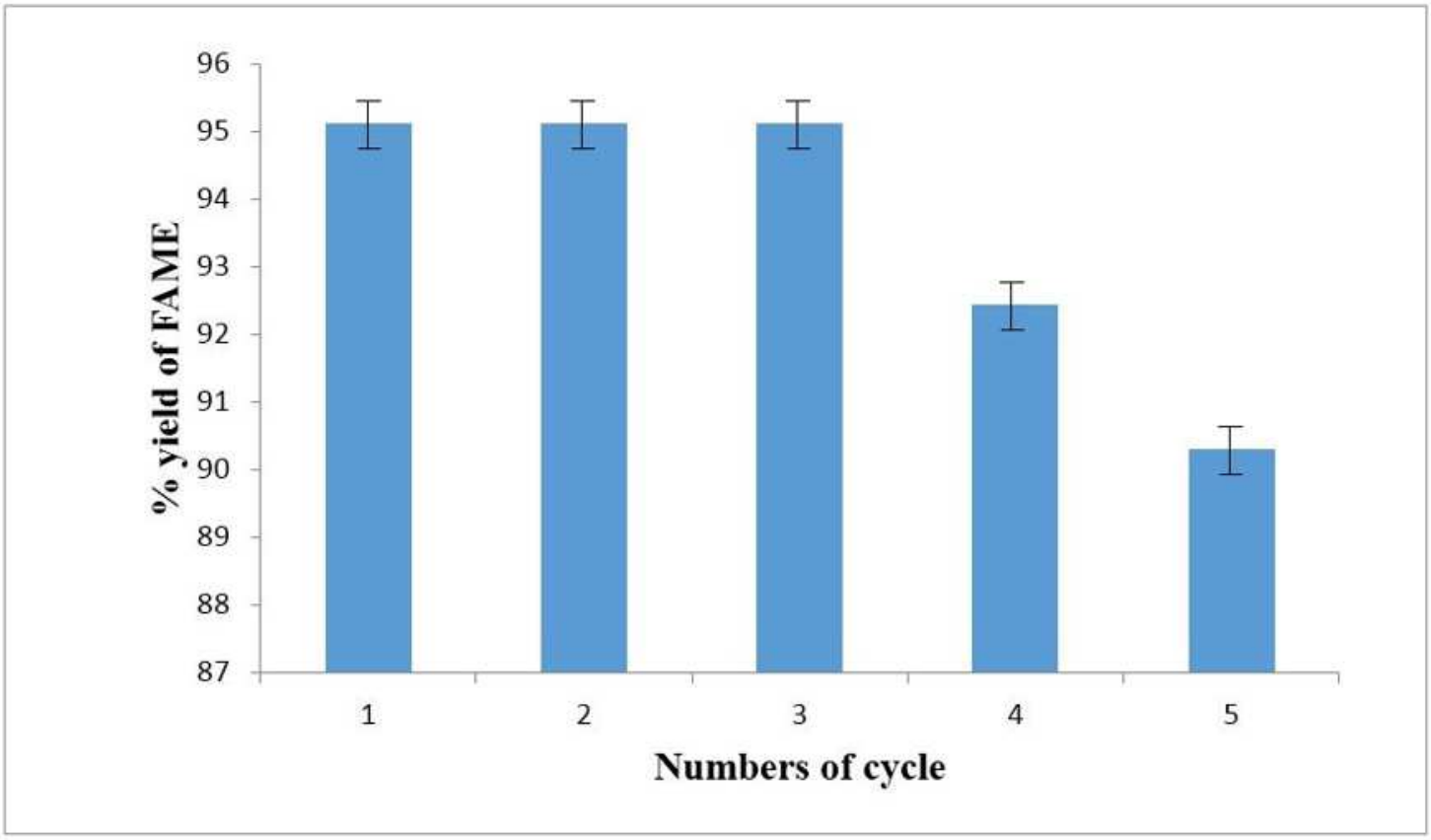

Figure 10

Reusability study of K-SC1.5 catalyst