Chapter 2

Materials and Methodology

2.1 Synopsis of methodologies

This chapter comprises the materials used and the methodologies acquired for the present work. The methods namely sol-gel auto combustion, polymer precursor auto combustion and wet impregnation were adopted for three new heterogeneous catalysts synthesis. The synthesized catalysts were characterized by various techniques namely TGA-DTA, XRD, XPS, SEM-EDAX and Hammett indicator titration. The activity of the newly synthesized catalysts in transesterification of waste cooking oil and castor oil was investigated through optimization and reusability study. Furthermore, the kinetic and thermodynamic studies were conducted to interpret the pathway of the reactions. The green parameter study helped to elaborate the "greenness" of the transesterification process catalyzed by the catalyst. The synthesized biodiesel samples were characterized by NMR (^{1}H and ^{13}C), GC-MS alongwith ASTM standard methods for physicochemical characterization.

2.2 Materials: Chemicals & Feedstocks

Chemicals**:** Potassium nitrate (99%), cerous nitrate (99%), tin (IV) chloride pentahydrate (98%), barium nitrate (99%), citric acid (99%), acetone (99.5%), methanol (ACS grade), ethanol (ACS grade), ammonium hydroxide (25% v/v), bromothymol blue (95%), nile blue (85%), neutral red (ACS grade), phenolphthalein (>98%), 2,4-dinitroaniline (98%), 4-nitroaniline (99%), d-chloroform (99.8% Atom D) were procured from Sigma Aldrich (Merck) Ltd, US; potassium hydroxide (KOH, 85%) was procured from HiMedia LPL, Mumbai, India. All chemicals were of analytical grade and were used without further purification.

Feedstocks: In this thesis work, waste cooking oil (WCO) and castor oil (CO) were used as feedstock for biodiesel production. WCO was collected from IIT-BHU cafeteria, Hostel canteens, hotel messes and restaurants near the IIT (BHU) campus. As the oil

contained impurities like food particles, moisture etc, so, a primary treatment was needed for better results. First, the collected WCO was filtered to eliminate the waste suspended food particles. During frying the food stuff, moisture contamination was incorporated into the WCO which might cause hydrolysis of triglyceride molecule present in oil. So, such moisture content was lessened by heating it at 80^{o}C for 3 h. But to complete removal of moisture, a definite amount of activated carbon was added into WCO and agitated at 70^{o}C for 1 h. After that, the oil was decanted into a collecting jar. Another feedstock, castor oil was purchased from Indian Biodiesel Corporation Baramati, Pune, Maharashtra (India). The important physicochemical properties of given feedstocks are disclosed in Table 2.1.

Table 2.1 Physicochemical properties of waste cooking oil and castor oil

Properties	**Waste cooking oil**	**Castor oil**
Color	Gardner 6 max	Gardner 4 max
Acid value (mg KOH/g oil)	1.53	1.2
Saphonification number (mg KOH/g oil)	204.6	182.36
Iodine number (mg I_2/g)	133.8	84.11
Calorific value (MJ/Kg)	38.44	36.47
Viscosity (mm^2/s) at 40^{o}C	68.21	232.4
Density (Kg/m^3) at 27^{o}C	906.2	959.3
Refractive Index	1.46	1.474

2.3 Synthesis routes of heterogeneous base catalysts

2.3.1 Sol-gel auto combustion method

Sol-gel method is a well known method for nano-catalyst synthesis. In this method, nitrates precursors of metals were weighed according to the required molar ratio, and were dissolved separately in double distilled water. Later, an optimum amount of citric

acid was dissolved in a 500 ml beaker kept on a hot-plate. In this method, citric acid was used for complexant material as well as fuel for the combustion process. The metal nitrate solutions were added one by one with continuous stirring. At this time, temperature of the hot-plate was raised to 80°C. After 1h of vigorous mixing, 25% ammonium hydroxide was added dropwise until the pH of the solution reached around 7. Due times, the solution became dense to denser and finally it was transformed into a citrate-nitrate sol which was slowly heated at 110°C to evaporate the excess water. After some time, it was turned into a gel. At that time, the stirrer was taken out, and the temperature of the gel was slowly increased to 300°C. Within 15 to 20 min the gel was turned into xerogel which was fired at 250 - 280°C. During the combustion process, ammonia, carbon monoxide, etc. gases were exhausted and the xerogel was burned with bright yellow flints. After 3 to 5 min of the combustion process, a black ash colored crude catalyst was obtained as product. Afterwards, the crude catalyst was crushed into powder and was calcined at high temperature in air muffle furnace for 6 h. Finally, the mixed metal oxide catalyst was obtained after calcination and it was stored in a desiccator to prevent from moisture contamination (Zhang et al., 2015).

2.3.2 Polymer precursor auto combustion method

This method is modified version of sol-gel auto combustion method. The stipulated amount of a metal nitrate precursor was dissolved in saturated aqueous solution. This aqueous solution was poured into an ultrasonicated aqueous solution of another metal oxide/ metal hydroxide. An equimolar aqueous solution of citric acid was appended as complexing agent to the metal precursor solution with continuous stirring on hot plate at 65°C and 600 rpm. Afterwards, 25% ammonia solution was added dropwise to the reaction mixture to adjust the pH of the medium around 7 which was essential for stabilizing the nitrate-citrate complex. Then, resulted sol was stirred vigorously at 110°C

to form gel. After the complete gelation, the entire reaction mixture was put for auto combustion at 280°C. The extensive burning of reaction mixture at this elevated temperature triggered the evolution of volatile carbonaceous products and nitrate degradation changing the color of dry gel to grey. Aftermath, the combustion product was undergone for calcination in muffle furnace for a definite time with heating rate of 10°C/min. Finally, the calcined catalyst was grinded into fine powder and was stored into a desiccator.

2.3.3 Wet impregnation method

This technique is widely used for synthesis of heterogeneous catalyst. At first, the saturated aqueous solution of active metal was prepared by dissolving a stipulated amount of its nitrate precursor into minimum amount of double distilled water. Afterwards, the saturated metal nitrate solution was added to an ultrasonicated metal oxide/ metal hydroxide with constant stirring at 80°C on hot plate. After 1h of mixing, the mixture was vigorously agitated at high temperature (above 100°C) for certain time period. The mixture became thick to thicker with time due to evaporation of water. At a time, the entire mixture turned into slurry which was placed in oven for drying. Thereafter, the dried slurry mixture was crushed into fine powder with the help of agate pestle and mortar, followed by calcination at high temperature to obtain the desired product. Finally, the product catalyst was stored in desiccator for using in characterization and application.

2.4 Catalyst characterization

Prepared catalyst samples were characterized by various techniques to ascertain the physicochemical properties. Figure 2.1 includes the images of instruments used for catalyst characterization. The instrumental specifications and technical methods are given in detailed as follows:

2.4.1 Thermogravimetric Analysis – Differential Thermal Analysis (TGA-DTA)

Thermogravimetric (TG) and differential thermal analysis (DTA) are thermo-analytic techniques that analyze the change of physicochemical properties of a material over temperature variation right from room temperature to the highest temperature of the instrument set for the scanning. Physical changes like vaporization, melting, crystallization, phase transformation, volume change by expansion and contraction etc, and chemical changes namely new product formation, oxidation, decomposition, chemisorption, corrosion, dehydration etc, can be explored by TG-DTA. In thermogravimetric analysis, the change in mass of the sample is recorded as a function of temperature at a definite heating rate in controlled atmosphere. The resultant plot of mass loss against temperature is known as thermogram. Differential thermal analysis registers the difference in temperature between the sample and thermally inert reference, as a function of programmed change of temperature. An endothermic event is assigned when the sample temperature is found to be lower than the reference; however, the opposite phenomenon is designated as an exothermic event. The area under the DTA peak defines the enthalpy (ΔH) of the thermal event (Gabbott, 2008). Thermal characterizations were monitored on EXSTAR TG/DTA 6300 instrument over temperature range 35-1300^{o}C with heating rate 10^{o}C/min under nitrogen atmosphere (200 ml/min). Alumina powder was taken as reference material.

2.4.2 X-ray diffraction (XRD)

X-ray diffraction is an authenticated non-destructive technique used to detect the crystal structure, phase, crystal orientation and defect of the studied material. In X-ray diffractogram, a prominent peak is evolved due to constructive interference of monochromatic X-ray beam diffracted by the atoms residing in a particular plane (hkl) at

a definite angular position 2θ (Borchert et al., 2005). A single peak signifies a particular plane in the crystal lattice; however, the entire peak pattern defines the lattice of the crystal. XRD pattern of the prepared catalysts was recorded on Rigaku Miniflex 600 powder diffractometer (Cu Kα monochromatic radiation with λ= 0.154nm) operating at 45 kV applied voltage and 15mAanode current. The diffractogram was registered within 2θ range of 10^{o}-90^{o} with 5^{o}/min scan rate and step width of 0.02^{o}. The Scan resolution and scan speed were kept 0.0002 and 4.0627 degree/min respectively. The resultant diffractogram was analyzed by the help of a database named 'Joint Committee of Powder Diffraction Standard (JCPDS)'.

2.4.3 X-ray photoelectron spectroscopy (XPS)

XPS is powerful surface-sensitive spectroscopic technique which provides qualitative and quantitative information regarding surface chemistry of a material. It can analyze the elements constituting the sample surface with very low limit of detection (the parts per thousand), empirical formula, chemical state, and electronic state of the elements present in sample. XPS can also manifest the density of different electronic states and oxidation states of a single element. XPS spectra is typically accomplished by exciting a portion of sample surface with mono-energetic Al kα X-rays causing photoelectrons to be emitted from the surface of the material at the average depth of 5 nm. An electron energy analyzer is used to measure the kinetic energy of the emitted photoelectrons. Binding energy and intensity of a photoelectron peak signify the elemental identity, chemical state, and quantity of a detected species. For this study, the XPS analysis was probed employing K-Alpha XPS analyzer of Thermo Fisher Scientific. The binding energy of C 1s i.e. 284.8 eV was considered as the reference peak for calibrating the binding energies of the corresponding elements present in the catalyst.

2.4.4 Scanning electron microscopy – Energy dispersive X-ray spectroscopy (SEM-EDAX)

SEM analysis is an impactful technique which provides high magnification image of surface topology of a solid object. Relatively low energy (0.5-30 kv) beam of focused electrons (primary) is bombarded in a regular manner over the specimen. The action of the electron beam stimulates emission of high energy backscattered electrons and low energy secondary electrons from the surface of the specimen. The surface topography of the sample at a gray scale is developed by measuring the intensity of secondary electrons as a function of the position of scanning primary electron beam. The intensity of backscattered electrons is recorded in EDAX detector as characteristic peaks of unique energy which can be correlated to the atomic number of the elements present in material. Hence, the type of elements and their compositional percentage in the material is obtained in form of elemental mapping. Surface morphology and elemental composition of synthesized catalysts were investigated on ZEISS EVO 18 SEM (Model 51-ADD0048) equipped with EDAX 51N1000-Ametek detector.

2.4.5 Textural characterization (BET-BJH)

Textural properties of a material include surface area, pore size, and pore volume are evaluated by BET-BJH analysis. The theory of BET (Brunauer Emmett Teller) analysis relates the multilayer physical adsorption of small gaseous molecules such as nitrogen on the porous solid as a function of relative pressure. It measures the specific surface area (in m^2/g) assimilating total external surface area and pore area available for adsorption. BET analysis also provides the information of surface porosity and particle size. The pore volume and the pore size distribution are evaluated from BJH adsorption-desorption plot. The adsorbed amount of vapor at a relative temperature close to unity in the pore informs

the total pore volume of solid sample (Brunauer et al., 1938). The textural characteristics of the synthesized catalyst samples were investigated by N_2 adsorption-desorption isotherm using Micrometrictics, ASAP 2020 V3.02 instrument (USA). The samples were degassed at 300°C for 3h to eliminate the impurities stick to the surface. Aftermath, the isotherms were recorded at -197°C.

2.4.6 Basic strength determination

Basic strength of the solid base catalysts is the number of basic sites present per gram of the sample. It was estimated by the Hammett indicator benzoic acid titration method. A series of Hammett indicators: neutral red (H_= 6.8), p-nitrophenol (H_= 7.2), thymol blue (H_= 8.9), phenolphthalein (H_= 9.3), Alizarin yellow (H_= 11.2), and 2,4-dinitroaniline (H_= 15.0), p-nitroaniline (H_= 18) were used. Firstly in the Hammett indicator experiment, 25 mg of catalyst sample was dispersed in 5 ml methanol. Then 2 to 3 drops of indicator solution were added to it under constant stirring. The catalyst solution adopted a definite colour depending upon the pH of the medium and the pK_a value of the aforementioned catalysts. After 30 min of stirring, the catalyst-indicator solution was left for 15 min to reach equilibrium. Finally, it was titrated against the 0.1M benzoic acid. The titer value indicated the number of basic sites present in 25 mg of catalyst. Thus, basicity was further calculated in millimoles per gram (Hammett and Deyrup, 1932).

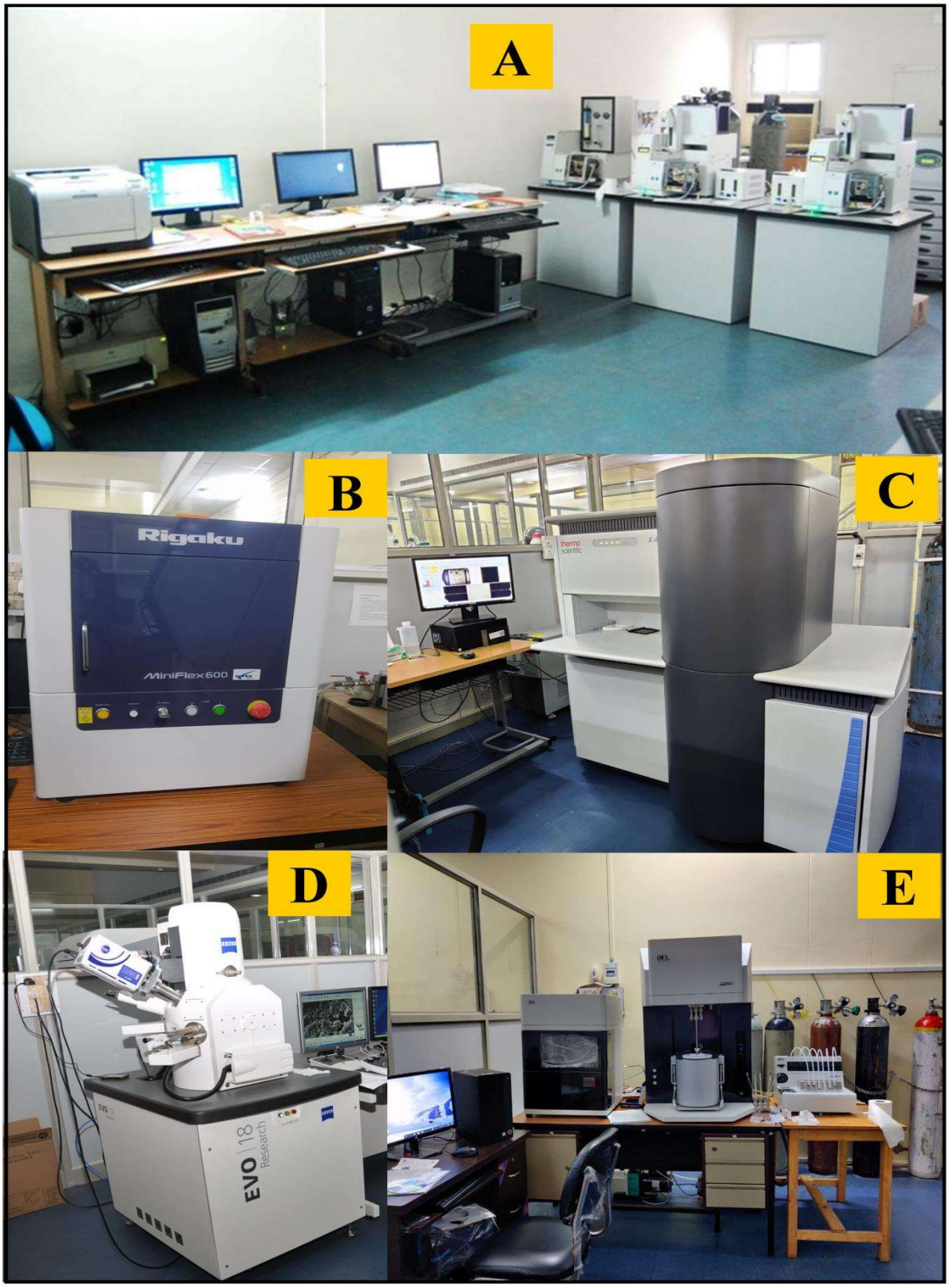

Figure 2.1 Image of instruments used for catalyst characterizations namely A) TGA-DTA, B) XRD, C) XPS, D) SEM-EDAX, E) BET-BJH

2.5 Biodiesel production via transesterification process

In present work, laboratory scale biodiesel production was carried out from waste cooking oil (WCO) and castor oil (CO) via one pot transesterification process (schematic diagram is shown as Figure 2.2). The acid values of WCO and CO were found to be 1.53 mg KOH/g and 1.2 mg KOH/g respectively. These acid values signified that both feedstocks had lower free fatty acid content which was under permissible limit for transesterification i.e. <2.5 mg KOH/g (ASTM 6751). Thus, WCO and CO were directly fed to the transesterification reaction without any pretreatment.

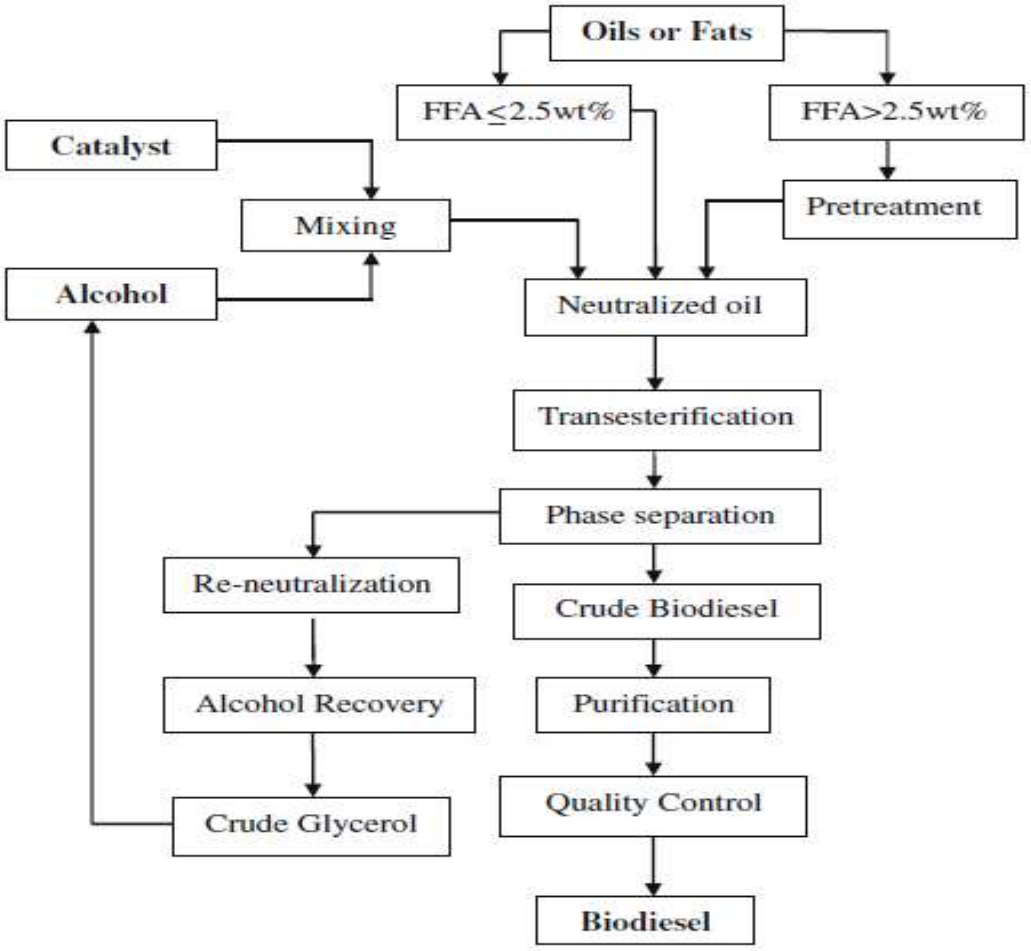

Figure 2.2 Schematic diagram of biodiesel production via one pot transesterification process

Lab scale biodiesel production was conducted in a temperature controlled batch reactor as shown in Figure 2.3. The transesterification reaction was executed in a 250 ml capacity of three necked round bottom (R.B) flask equipped with a reflux condenser, rotation controlled mechanical stirrer and a thermometer. The whole assembly was submerged into the water bath. A required amount of catalyst was first dispersed into a definite amount of methanol in the R.B at room temperature for 15 min. Then maintaining oil to methanol molar ratio, a calculated amount of oil was poured into the flask and stirred at optimum temperature for optimum reaction duration under reflux condition. The important reaction parameters as catalyst activation temperature, oil to methanol molar ratio, catalyst weight %, reaction temperature and time were optimized along with catalyst endurance by following the aforementioned reaction procedure.

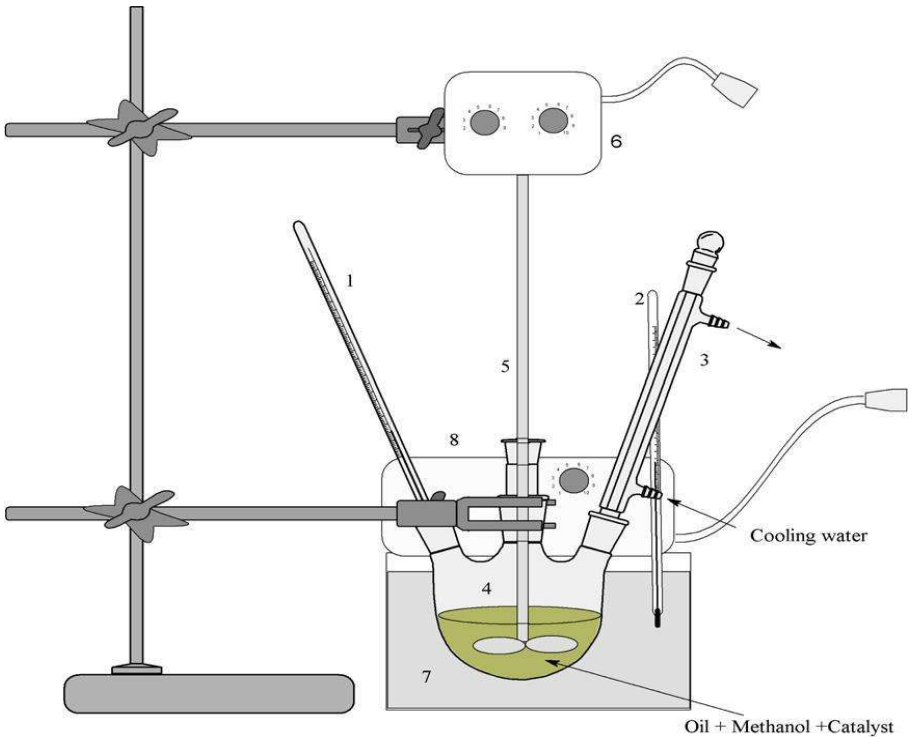

Figure 2.3 The arrangement of lab scale batch reactor for biodiesel production via transesterification process

After completion the reaction, the product mixture was transferred into a separating funnel. A day after, the product mixture was settled down and got separated in three distinct phases according to their density. Bottom layer was the solid catalyst, middle layer contained glycerol and the upper layer was constituted by FAME/ biodiesel and excess methanol. Thereafter, three phases were brought out one by one. Catalyst was washed subsequently by methanol and ethanol and reused in 2nd cycle, whereas byproduct glycerol was stored to use in value-added product synthesis. The synthesized biodiesel was kept in hot air oven at 65-70^{o}C for 1 day to get rid of the excess methanol present in FAME. Finally, the product FAME was characterized, quantified and stored for emission test.

2.6 Process optimization

To achieve the best catalytic performance of the synthesized catalysts in biodiesel production, various reaction parameters including catalyst preparation variables and transesterification reaction variables were optimized. Catalyst preparation variables namely atomic ratio of the metals, calcination temperature, and calcination time were optimized considering their individual significant contribution in transesterification process. Balat and Balat (2010) reported that the most influential transesterification reaction variables are oil to methanol molar ratio, catalyst weight %, reaction temperature, time, moisture content and free fatty acid content of feedstock. As both the feedstock had negligible amount of moisture and FFA, so these two factors were considered as insignificant variables for transesterification reaction of WCO and CO. For process optimization, manual 'One Variable at a Time' (OVAT) methodology was followed. One of such aforementioned variables regarding a particular catalytic transesterification was optimized by varying the parameter over a range keeping other variables constant. For K modified ceria oxide catalyst, the catalyst optimization process

was carried out over a range of K/Ce atomic ratio (0-3 with 0.5 increment) and catalyst activation temperature (600-1000°C with 100°C increment); however, the transesterification reaction variables were optimized over a précised range of oil to methanol molar ratio (1:8-1:18), catalyst weight % (0.5-3 wt%), temperature (45-75°C), and time (15-150 min). For K-Sn oxide catalyst, the optimization process was accomplished at following reaction circumstances over a definite range: activation temperature of the catalyst (500°C to 900°C), activation time of the catalyst (1h to 6h at 800°C), oil to methanol molar ratio (1:4 to 1:24), catalyst weight % (0.5wt% to 4 wt%), temperature (45°C to 75°C), and time (5min to 50 min). For Ba-Sn oxide catalyst, the parametric optimizations were conducted over a range of following variables: Ba:Sn atomic ratio (1:1, 2:1, 1:2), catalyst activation temperature (550°C to 950°C),), oil to methanol molar ratio (1:4 to 1:24), catalyst weight % (0.5wt% to 3 wt%), temperature (45°C to 75°C), and time (5min to 35 min).

2.7 Reusability of catalyst

One of the important reasons to choose heterogeneous catalyst over homogeneous catalyst is its reusability in biodiesel production. Reusability tests were conducted at the corresponding optimum reaction conditions for WCO and CO transesterification using a particular catalyst. To investigate the endurance capacity of the synthesized catalysts in transesterification reaction, reactivation of the catalysts was required after each catalytic run. Such reactivation was acquired by the following steps: **Step 1-** after completion of the transesterification reaction, the catalyst was recovered from the reaction mixture by easy filtration method, then washed subsequently by methanol and ethanol. **Step 2-** the washed catalyst was put into an air dry oven at 100°C for 8h to remove the solvent molecules from the catalyst surface. **Step 3-** the dried catalyst was recalcined at 600°C for 2 h to decompose the residual organic species (triglyceride and glycerol) which were

still stuck to the pores after washing. In this thesis, the newly synthesized catalysts namely K modified ceria oxide, potassium tin oxide and barium tin oxide were recycled for five consecutive runs of WCO and CO transesterification.

2.8 Kinetics and thermodynamics

The kinetic and thermodynamic parameters of transesterification reaction of WCO and CO using heterogeneous catalyst were investigated on the basis of modeling and theories as discussed below:

2.8.1 Determination of rate constant

The methyl ester formation is constructed by three simultaneous reversible reactions as shown below:

$$TG + M \leftrightarrow DG + ME \quad (2.1a)$$

$$DG + M \leftrightarrow MG + ME \quad (2.1b)$$

$$MG + M \leftrightarrow GL + ME \quad (2.1c)$$

Where, TG, DG and MG define triglyceride, diglyceride, monoglyceride respectively. M signifies Methanol; whereas the product GL and ME represent glycerol and methyl ester or biodiesel respectively.

The final balanced chemical reaction can be represented as:

$$TG + 3M \leftrightarrow GL + 3ME \quad (2.2)$$

The heterogeneous transesterification of oil is proposed to occur in three steps namely adsorption, surface reaction and desorption (Putra et al., 2018).

Adsorption

During transesterification, triglycerides are converted to methyl esters on catalyst surface at a higher molar concentration of methanol than the stoichiometric ratio. This demonstrates that TG is definitely adsorbed on to the catalyst surface.

$$TG + S \leftrightarrow TG.S \quad (2.3)$$

Where, S and TG.S mean the vacant sites of the catalyst surface and adsorbed triglyceride at active sites of the catalyst. The rate of adsorption of triglyceride can be described as:

$$\text{Rate of adsorption } r_{ad} = K_a[TG][S] - K_{-a}[TG.S] \quad (2.4)$$

Surface reaction

The adsorbed triglyceride (TG.S) interacts with excess methanol to synthesize methyl ester and glycerol as a byproduct. Glycerol tends to adsorb at the catalyst surface; whereas, methyl ester can be released instantly.

$$M + TG.S \leftrightarrow GL.S + ME \quad (2.5)$$

Here, GL.S is the adsorbed glycerol on active sites. The rate of surface reaction can be written as

$$\text{Rate of the surface reaction } r_s = K_s[M][TG.S] - K_{-s}[GL.S][ME] \quad (2.6)$$

Desorption

Desorption of glycerol can be represented as:

$$GL.S \leftrightarrow GL + S \quad (2.7)$$

The rate of desorption of glycerol has been shown below:

Rate of desorption $r_d = K_d[GL.S] - K_{-d}[GL][S]$ (2.8)

The surface reaction step is considered as the slowest and the rate-determining step for the heterogeneous transesterification reaction. So, rate of the surface reaction ultimately describe the rate of the overall transesterification reaction. The total concentration of surface [TS] can be represented as the sum of vacant surface concentration, adsorbed triglyceride concentration [TG.S] and adsorbed glycerol concentration [GL.S].

i.e. $[TS] = [S] + [TG.S] + [GL.S]$ (2.9)

The surface rate equation 2.6 can be rearranged by substituting the terms [TG.S], [GL.S], [S] and it can be expressed as:

$r_s = K_A.K_s[TS]\ ([TG][M] - [GL][ME]/K_{-s})/(1+ K_A[TG] +[GL]/K_D)$ (2.10)

K_A & K_D are the equilibrium constant of adsorption and desorption respectively. In case of glycerol, the rate of adsorption is very less, and the rate of desorption is very high. Both the terms $K_A[TG]$ & $[GL]/K_D$ are considered to be zero. Moreover, in transesterification [M] >> [TG], so the change in concentration of methanol is considered to be insignificant. [TS] is a constant value for a given catalyst. Therefore, the final rate equation can be set as:

$r_s = d[TG]/dt = k[TG]$ (2.11)

Where, k implies the final rate constant which is equal to $K_A \times K_s \times [TS] \times [M]$

Now integrating equation 2.11, under the limiting condition as $[TG]_0$ to $[TG]_t$ at time 0 to t, we get:

$-\ln([TG]_t/[TG]_0) = k \times t$ (2.12)

From mass balance,

$$X_{ME} = 1 - ([TG]_t/[TG]_0) \quad (2.13)$$

$$So, [TG]_t = [TG]_0 \times (1 - X_{ME}) \quad (2.14)$$

X_{ME} defines methyl ester conversion. Integrating the equation 13 in terms of X_{ME} leads to:

$$-\ln(1 - X_{ME}) = k \times t \quad (2.15)$$

Thus, plotting $-\ln(1-X_{ME})$ vs t (min), rate constant k can be determined from the slope of the graph. In this study, at a constant temperature, a series of FAME conversions were evaluated over a time period with a definite time interval. Then, resultant data was processed according to the equation 2.15 and plotted in Origin. The slope of the linear fit informed the rate constant at the particular temperature (Encinar et al., 2018).

2.8.2 Determination of activation energy and frequency factor

The relation between rate constant (k, min^{-1}) and the reaction temperature (T in Kelvin) can be shown by Arrhenius equation (Chen et al., 2020):

$$k = A \times \exp(-E_a/RT) \quad (2.16)$$

$$or, \ln k = \ln A - E_a/RT \quad (2.17)$$

Where, A is the Arrhenius constant or frequency factor in min^{-1}, E_a is activation temperature in $kJ.mol^{-1}$, and R is the gas constant (8.314×10^{-3} $kJ.K^{-1}.mol^{-1}$). The slope and intercept of the plot of lnk vs 1/T help to derive reaction activation energy and frequency factor respectively.

2.8.3 Evaluation of enthalpy of activation, entropy of activation and Gibb's free energy of activation

Eyring – Polanyi equation for Gibb's free energy of activation leads to:

$$k = k_b T/h \times \exp(-\Delta G^{\#}/RT) \quad (2.18)$$

The fundamental thermodynamics equation for calculating Gibb's free energy of activation $\Delta G^{\#}$ can be expressed as:

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \quad (2.19)$$

The equation 2.18 can be written in terms of enthalpy of activation $\Delta H^{\#}$ and entropy of activation $\Delta S^{\#}$ as follows:

$$k = k_b T/h \times \exp[(-\Delta H^{\#} + T\Delta S^{\#})/RT) \quad (2.20)$$

$$\text{or, } \ln(k/T) = [\ln(k_b/h) + (\Delta S^{\#}/R)] - (\Delta H^{\#}/RT) \quad (2.21)$$

Where, k_b = Boltzmann constant (1.38×10^{-38} $J.K^{-1}$), h = Planck constant (6.626×10^{-34} J.s). $\Delta H^{\#}$ and $\Delta S^{\#}$ can be evaluated from the slope and the intercept of the linear regression plot of ln(k/T) Vs 1/T accordingly. Determining both the values of $\Delta H^{\#}$ and $\Delta S^{\#}$, the value of $\Delta G^{\#}$ can also be evaluated by using equation 2.19.

2.9 Determination of 'Green factors' of the process

Under optimized reaction conditions, the transesterification reactions of WCO and CO using solid base catalysts can be evaluated with respect to green parameters such as yield, turnover frequency (TOF), environmental factor (E- factor) and process mass index (PMI). These factors ultimately decide whether the process is green or not.

2.9.1 Yield of biodiesel

Yield of the product biodiesel can be defined as the following equation (Vicente et al., 2007):

$$Yield\ (\%) = \frac{weight\ of\ produced\ biodiesel\ (g)}{weight\ of\ WCO\ used\ \ (g)} \times 100 \quad (2.22)$$

2.9.2 Turnover frequency (TOF)

It is defined as number of moles of the product has been produced at single basic site per unit time (Abdul et al., 2015). Number of basic sites present in catalyst can be determined from the basicity of the catalyst which is considered in millimoles per gram. Time corresponds the optimized reaction duration in second.

$$Turnover\ frquency = \frac{moles\ of\ biodiesel}{basicity \times 10^{-3} \times time\ (s)} \quad (2.23)$$

2.9.3 Environmental- factor (E- factor) and Process Mass Index (PMI)

The extent of cleanness is subjected to the amount of waste generated during the process. The pathway produced lower amount of waste would be considered as cleaner or greener pathway. Thus, the cleaner pathway of the transesterification process of WCO and CO using different solid base catalysts were derived by calculating E-factor and PMI of the corresponding process using the equations given below (Yadav and Sharma, 2019):

$$E - factor = \frac{Produced\ waste\ mass\ in\ g}{Produced\ biodiesel\ mass\ in\ g} \quad (2.24)$$

$$PMI = \frac{Total\ mass\ used\ in\ transesterification\ process}{Produced\ biodiesel\ mass\ in\ g} \quad (2.25)$$

Environmental factor (E-factor) is illustrated as weight of waste produced per weight of product or biodiesel (in gram); whereas, PMI defines the total mass used in

the process per gram of biodiesel production. In transesterification reaction, glycerol and unreacted triglycerides have been considered as waste product. Other substances like solvents and catalyst were excluded from the list of waste; this is because the solvents were distilled and reused in next cycle; similarly catalyst was also recovered and recycled for next batch runs.

2.10 Biodiesel characterization

The product biodiesel was inspected through Proton Nuclear Magnetic Resonance (^{1}H-NMR) spectroscopy, Carbon Nuclear Magnetic Resonance (^{13}C-NMR) Spectroscopy, Gas chromatography-Mass Spectroscopy (GC-MS). The images of instruments used in biodiesel characterization is given in Figure 2.4.

2.10.1 Proton and Carbon Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR and ^{13}C-NMR)

Nuclear Magnetic Resonance (NMR) is a potential analytical tool to investigate the molecular structure of the organic material. ^{1}H-NMR informs the different types of protons present in the methyl esters, whereas, ^{13}C-NMR suggests the different type of carbons present in the methyl esters (Satyarthi et al., 2009). Both the NMR spectra of the methyl ester can be correlated to confirm the molecular structure of the product biodiesel. In present study, ^{1}H-NMR and ^{13}C-NMR analysis of biodiesel were performed on BRUKER 500 (advance III HD) instrument with scan rate of 32 for 512 scan. $CDCl_3$ and tetramethylsilane were used as solvent and internal standard respectively. The quantitative analysis in terms of FAME conversion was accounted by ^{1}H NMR technique using the following equation (Birla et al., 2012):

$$\text{FAME conversion (\%)} = \frac{2A_{OCH_3}}{3A_{\alpha-CH_2}} \times 100 \qquad (2.26)$$

Where, A_{OCH_3} defines the integration of signal associated with the methoxy hydrogen and $A_{\alpha-CH_2}$ ascertains the integration of the signal associated with the α-methylene hydrogen.

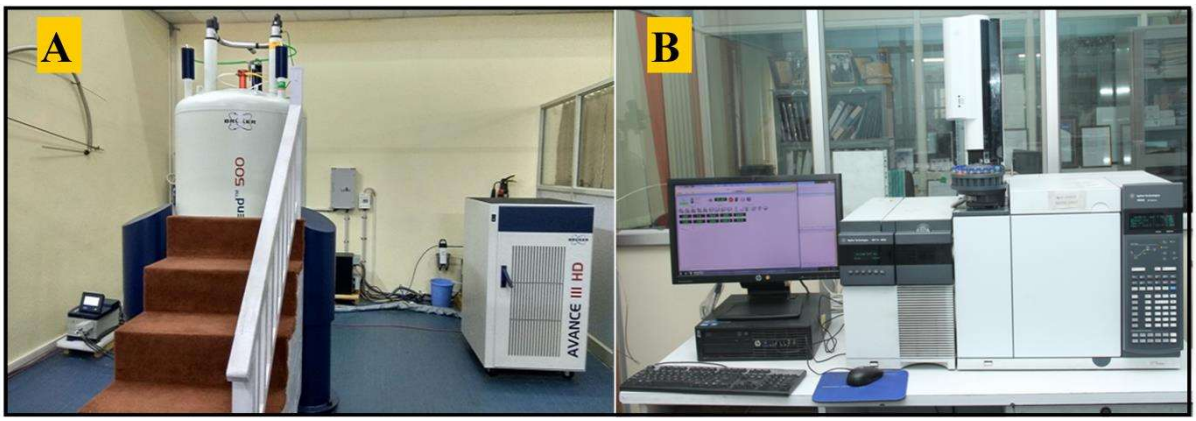

Figure 2.4 Image of instruments used for biodiesel characterization A) NMR and B) GC-MS

2.10.2 Gas chromatography - Mass Spectroscopy

The Gas chromatography-Mass Spectroscopy is powerful analytical technique to identify the organic composition of an analytical mixture. The constituent fatty acid methyl esters (FAME) of waste cooking oil biodiesel and castor oil biodiesel were qualitatively and quantitatively analyzed by GC-MS. Such compositional analysis of these two feedstocks was performed on Agilent 6890N gas chromatograph equipped with Agilent 5977 A mass spectrometer. The gas chromatograph was outfitted with an Agilent Db-225 capillary (30 m × 25 mm × 0.25µm). The column temperature was set to 160°C for 2 min. Then it was increased to 230°C at 5°C/min. At 230°C, it was held for 20 min. Nitrogen, as carrier gas, was passed into the column with 1.0 ml/min flow rate. Inlet temperature was fixed at 250°C, and the split ratio was maintained 50:1. Flame ionization detector (FID) was used, and the detector temperature was kept up 280°C. Supelco 37 Component FAME Mix (CRM 47885) was used as standard material. The obtained data were compared with

NIST database for identification of fatty acid methyl esters in synthesized biodiesel samples.

2.10.3 Physicochemical characterizations

The physicochemical properties such as acid value, density, kinematic viscosity, cetane number, calorific value, flash point, pour point, and cloud point were investigated by the following procedures described by American Society for Testing and Materials (ASTM) standards. The quality of biodiesel depends on composition of methyl esters, type of production route followed and purity of the sample. ASTM has assigned permissible limit of various physicochemical properties for biodiesel to use in C.I. engines. Thus, it is mandatory for the researchers as well as producers, that the quality of the product biodiesel should belong under permissible limit; then only the industry level production will be permitted. The ASTM standard methods used for evaluating the physicochemical properties are mentioned in Table 2.2 with the assigned permissible limits.

2.10.3a Acid value

The acid value is defined as the number of milligrams of potassium hydroxide (KOH) needed to neutralize the free fatty acids present in 1g of oil or fat. High free fatty acid content in biodiesel may cause corrosion of internal combustion engine and fuel supply system. ASTM-D6751 has mentioned that the standard acid value for biodiesel is less than equal to 0.5 mg KOH/g.

2.10.3b Density

The ratio of mass to volume is density expressed in g/cm^3. The engine performance depends on compression ratio (CR) which is defined as the ratio of maximum to minimum volume in the cylinder of an internal combustion engine. The lower density fuel

has higher CR value, so it will show better performance than higher density fuel. Biodiesel is denser than conventional petrodiesel due to higher molecular weight; so, its application has been encouraged in form of blending with petrodiesel. The density of product biodiesel was determined as per ASTM D4052 standard method using digital densitometer.

2.10.3c Kinematic viscosity

Kinematic viscosity is defined as the ratio between the dynamic viscosity and density of the fluid. It affects the atomization of fuel in combustion chamber. Incomplete atomization causes carbon deposition inside the engine and fuel injector, and it also causes a difference in injection timing and spray patterns during fuel ignition. Poor atomization is more observed in case of higher kinematic viscosity fuel. Following ASTM D445 testing method, kinematic viscosity of the synthesized biodiesel was estimated employing Redwood viscometer.

2.10.3d Cetane number

The potential of fuel is typically characterized by cetane number. Higher cetane number implies lower ignition delay. Ignition delay is the time difference between start of fuel injection and start of its combustion. Shorter ignition delay is appreciated for better fuel-air mixing, lower NO_x emissions and lesser occurrence of knocking phenomena in combustion process. The cetane number of synthesized biodiesel was determined as per ASTM D976 test method using the following equation:

$$CN = 454.74 - 1641.416D + 774.74D^2 - 0.554B + 97.803 (\log B)^2 \quad (2.27)$$

Where, D and B are density and mild-boiling temperature of the biodiesel.

2.10.3e Calorific value

Calorific value of a fuel is the amount of energy released in form of heat during combustion of unit quantity of fuel. Density is inversely proportional to energy content of fuel and it is directly proportional to the fuel consumption. Biodiesel has comparatively lower calorific value than the conventional diesel fuel owing to higher density. In order to gain the same power, biodiesel is required in larger amount compare to petrodiesel. High calorific value signifies better combustion of the fuel which facilitates the engine performance. Calorific value of the synthesized biodiesel was evaluated by following ASTM D240 testing method using bomb calorimeter.

2.10.3f Flash point and fire point

The flash point of a flammable liquid is the lowest temperature at which the vapor of the fuel flashes when it is exposed to an open flame; whereas, a slightly higher temperature, the fire point is defined as the lowest temperature at which the burning becomes continuous after 5 to 6 seconds of being ignited. High flash point and fire point is advantageous for handling safety, storage, transportation safety and avoiding unexpected explosion during combustion. Flash point and fire point were determined as per ASTM D93 standard test method using Pensky-Martens closed cup tester.

2.10.3g Cloud point and pour point

Cold flow property of fuel is denoted in terms of cloud point and pour point. Cloud point is the temperature below which wax formation starts due to solidification of saturates. The pour point is the temperature at which the liquid loses its fluidity and becomes semi-liquid. As in biodiesel, saturated fatty acids are present in significant amount; it shows higher cloud point and pour point compare to diesel. Kerosene, ethanol etc. are used as

additives in biodiesel to improve the clod flow property. Cloud point and pour point were determined by adopting ASTM D2500 and ASTM D97standard test method respectively.

Table 2.2 Physicochemical characterization of biodiesel

Parameters	Unit	ASTM test method used	ASTM-6751 biodiesel	Testing Apparatus
Acid value	mgKOH/g	D 664	<0.5	Titrimetric method
Density (at 40°C)	$g.cm^{-3}$	D 4052	0.86-0.90	Pycnometer
Kinematic Viscosity (at 40°C)	mm^2/s	D 7110	1.9 to 6.0	Red wood viscometer
Cetane number	-	D 613	47	Ignition quality tester
Calorific value	MJ/Kg	D 240	35	Bomb calorimeter
Flash point and Fire point	°C	D 93	100 to 170 130 to 210	Pensky-Martens closed tester
Pour point	°C	D 97	-15 to 16	Manual
Cloud point	°C	D2500	-3 to 12	Manual