Chapter-3

Materials and Methodology

This chapter describes the materials used and the detailed experimental procedure adopted in the present work. A brief introduction to the various analytical tools used for the characterization of nanoparticles, oils, and worn surfaces are discussed.

3.1. Materials

3.1.1. Base oil

The present work aims to motivate and develop the potential biolubricants for industrial and automotive use. Therefore, a variety of the vegetable based biolubricants has been investigated in this study to evaluate the tribological properties like antiwear, antifriction, weld load and load carrying capacity in close contact situations. Most of the base oils were analytical grade and few extracted by the seeds using mechanical expeller. The details of selected base oils used for experimentation are presented in Table 3.1:

Table 3.1. Details of explored biolubricants.

Base oil	Grade	Manufacturer	Measured parameters
Castor	Analytical	Hi-Media, Mumbai	η_0 : 0.280 and PP: -33
Sunflower	Extracted	-	η_0 : 0.076 and PP: -18
Rapeseed	Extracted	-	η_0 : 0.089 and PP: -29
Olive	Analytical	QualiChem Laboratories, Nagpur	η_0 : 0.087 and PP: -9
Neemseed	Analytical	QualiChem Laboratories, Nagpur	η_0 : 0.033 and PP: -12
Cottonseed	Analytical	QualiChem Laboratories, Nagpur	η_0 : 0.063 and PP: -9
Sesame	Analytical	QualiChem Laboratories, Nagpur	η_0 : 0.065 and PP: -8
Note: $\boldsymbol{\eta_0}$: dynamic viscosity (at 30°C; N-s/m^2), PP : pour point (°C)			

3.1.2. Chemicals

A variety of chemicals (analytical grade) was used in the synthesis of the nanoparticle, base oil modification, as a dispersant, etc. and presented in Table 3.2.

3.1.3. Additives

Many additives were added to the base oils (either modified or unmodified) in a very small range of concentration (vary from 0.1 to 1.0%w/v) to investigate the tribological performance. The list of the used additives given in Table 3.3.

Table 3.2. List of the analytical grade chemicals used in the present study.

Chemical Name	**Chemical formula**	**Used for**	**Manufacturer**
Calcium Nitrate Tetrahydrate	$Ca(NO_3)_2 . 4H_2O$	Synthesis	Merck India
Copper Nitrate Trihydrate	$Cu(NO_3)_2 . 3H_2O$	Synthesis	Merck India
Titanium Isopropoxide	$C_{12}H_{28}O_4Ti$	Synthesis	Spectrochem, Mumbai
Citric Acid	$C_6H_8O_7$	Synthesis	Merck India
Formic acid (98%)	CH_2O_2	Oil modification	Avra Chemicals
Hydrogen Peroxide (30%)	H_2O_2	Oil modification	Avra Chemicals
Sulfuric Acid	H_2SO_4	Oil modification	Avra Chemicals
Diethyl Ether	$(C_2H_5)_2O$	Oil modification	SRL Chemicals
Sodium Dodecyl Sulphate	$NaC_{12}H_{25}SO_4$	Dispersant	SRL Chemicals
Deuterated chloroform	$CDCl_3$	Sample preparation for NMR	Merck India
Acetone	$(CH_3)_2CO$	Surface cleaning	Finar Limited

Table 3.3. List of additives used in the oil.

Additive Name	Chemical formula	Manufacturer	Nature	Remarks
Zinc dialkyldithiophosphates (ZDDP)	$Zn[(S_2P(OR)_2]_2$	Afton Chemical Ltd., Richmond	Liquid	Multifunctional & commercial use
Calcium-copper-titanate (CCTO)	$CaCu_3Ti_4O_{12}$	-	Ceramic	Synthesized
Copper oxide	CuO	Avansa Technology and services, Kanpur	Ceramic	Purchased
Ceria or cerium oxide	CeO_2	Avansa Technology and services, Kanpur	Ceramic	Purchased
Polytetrafluoroethylene (*PTFE*)	$(C_2F_4)_n$	Sigma-aldrich	polymeric	Purchased

3.1.4. Synthesis of calcium-copper-titanate nanoparticles

There are various synthesis methods to produce nanoparticles (i.e. physical vapor deposition, chemical vapor deposition, sol-gel method, thermolysis and solution combustion method). In the present work, sol-gel approach was adopted for the synthesis of CCTO nanoparticles, which is one of the economical methods.

Sol-gel method:

In the sol-gel process, as the name indicates, a stable colloid solution (called as *sol*) is converted into gel material. In general, the sol is a liquid solution containing solid particles or chemicals (inorganic salt or a metal alkoxide), which is obtained by hydrolysis and partial condensation of precursors. Further condensation of sol, forms diphasic material (called as a *gel*). If deionized water used as a solvent, then it is known as an aqua sol or aqua gel.

Thereafter, the gel was dried either by evaporation drying (termed as xerogel) or supercritical drying (termed as aerogel) to obtain a solid product.

Synthesis:

The calculated amount of analytical grade metal nitrates powder was mixed in a beaker to form stoichiometric nitrate solution. The solution of titanium isopropoxide and a citric acid equivalent to metal ions prepared in another beaker in a required calculated amount. Both solutions were mixed, and heated up to 90-100°C and stirred at 1200 rpm through magnetic stirrer cum hot plate. This process continued till the blue gel is obtained.

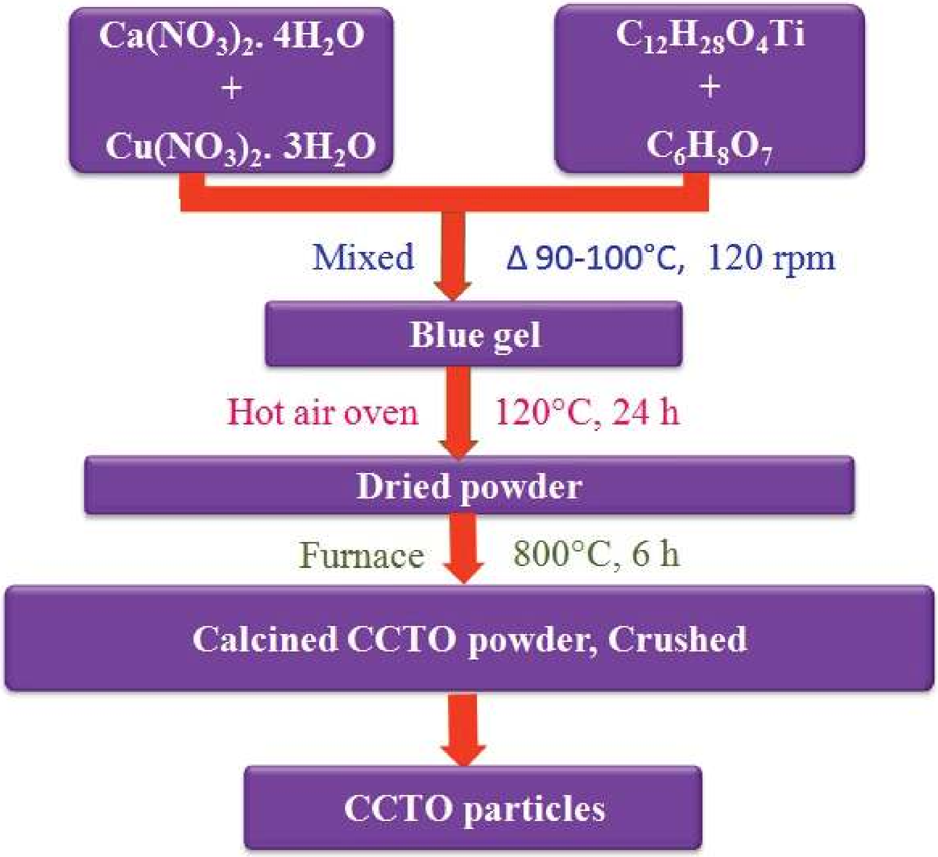

Figure 3.1. Flow diagram for synthesis of CCTO.

The obtained blue gel was dried in hot air oven at 120°C for 24 hours. The dried powder was then calcined in the muffle furnace for 6 hours at 800°C and finally crushed through pestle and mortar to get CCTO powder. Figure 3.1 shows the synthesis process in the form of the flow chart.

3.1.5. Test specimen

AISI 52100 alloy steel balls were used to examine the tribological behaviour of various lubricant compositions. The size, hardness and roughness of the steel balls were 12.7 mm, 59-61 HRC, and 17 nm (r.m.s.) respectively. The composition of the steel ball summarized in Table 3.4.

Table 3.4. Composition of AISI 52100 steel balls.

Elements	C	Si	Mn	P	S	Cr	Fe
Content (%)	0.95	0.15	0.24	0.02	0.018	1.3	97.3

3.2. Experimentation: Details of tribo-tester and test procedure

The ASTM standards have been followed to evaluate the different tribological properties of the lubricating oils. Table 3.5 enumerates the summary of ASTM standard which has been followed in the present work for conducting different types of tribo-test (such as antiwear, extreme pressure and coefficient of friction test) by using four-ball tester (manufacturer DUCOM Instruments Pvt. Ltd., Bengalore, India).

The test procedure was as follows:

- Before starting of the tribological test, all four balls, ball-pot, splash guard and collet (also called as ball chuck) were cleaned properly using acetone by ultrasonication to remove foreign contamination. After cleaning, all the parts were dried and wiped with fresh tissue paper.

- One of the balls was fixed in the rotating spindle via collet.
- Three cleaned balls were fixed in the stationary ball pot using a special wrench supplied by the equipment manufacturer.
- Approximately 10 ml of the test oil was poured into the ball pot and it must cover the top surfaces of the lower balls.
- The oil filled ball pot placed slowly inside the test chamber. Then test load of 392 N was applied slowly using the dead weights.
- Thereafter heater was attached to the ball pot to maintain the oil pre-set temperature to 75°C using the controller unit.
- After reaching the pre-set temperature, the test was started at a spindle speed of 1200± 60 r.p.m. Winducom 2010 software also started simultaneously with the motor to record the data.
- After completion of the test, the test rig turns off automatically. Thereafter, the heater was removed.
- The tested oil was drained and the tested ball surface was wiped by using fresh tissue paper. The ball pot containing three balls placed under image acquisition microscope system in unclamped condition.
- The wear scar sizes on the three lower balls were directly measured with the microscope. And, the average was reported as mean wear scar diameter (WSD; in μm).

- Each test has been repeated at least three times to obtain repeatability in the tribological results.

Table 3.5. ASTM standard followed for evalauting the tribological properties of different lubricant compositions by using four ball tester.

Standard	Load (kgf)	Duration (sec)	Temperature (°C)	Speed (rpm)
ASTM D4172 (Antiwear test)	40	3600	75±2	1200 ± 60
ASTM D2783 **(Extreme-pressure test)**	6 8 10 13 16 20 24 32 40 50 63 80 100 126 160 200 250 315 400 500 620 800	10 At each load	27 ± 8	1760 ± 40

Figure 3.2 represents the actual experimental set-up and the detailed arrangement of balls, and load application. The representative contact between the all four balls has depicted in Figure 3.2 (b). And, Figure 3.2(c) represents typical SEM image of top rotating worn ball. Both adhesive and abrasive wear were revealed on the worn track.

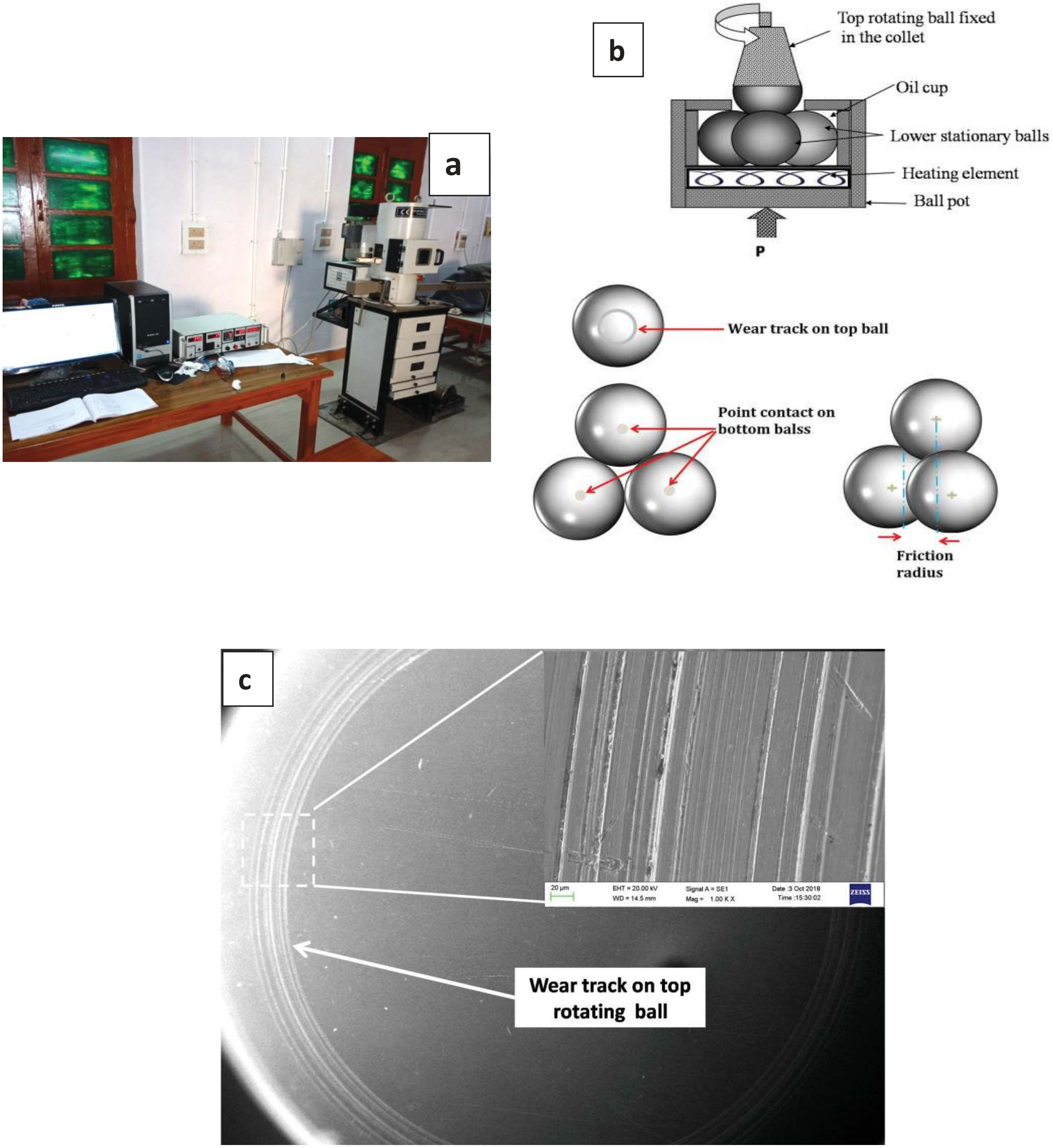

Figure 3.2. Image of; (a) actual experimental set-up and (b) schematic arrangement of all four balls and (c) SEM of top rotating ball.

- ***Calculations of load distribution and film thickness for four-ball tester***

The contact geometry was recognized as point contact in case of for ball tester, as presented in Figure 3.2 (b), and it follows the Hertzian contact criteria. The calculated Hertzian diameter in case of four-ball tester was 405.4 µm (detailed calculation presented in Appendix-A). The contact angles between balls were 35.265° as per ASTM standard. For the antiwear test, the applied load was 40 kgf (or 392 N) and Eq. 3.1 used for the calculation of actual contact load;

$$P = N \text{ Cos } (35.265^\circ) \qquad (3.1)$$

Where P: applied load, N: total actual contact load on three lower balls

One-third of the total contact load "N" has been uniformly distributed among three lower balls (i.e., W = N/3). The maximum contact pressure (i.e., Hertz stress) calculated by using Eq.3.2 and the mean contact pressure is two-third of maximum contact pressure. Eq.3.3 and 3.4 are supporting equations of Eq.3.2.

$$p_0 = \frac{1}{\pi}\left[\frac{6WE'^2}{R^2}\right]^{1/3} \qquad (3.2)$$

$$\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2} \qquad (3.3)$$

$$E' = \frac{2E_1E_2}{E_2(1-\nu_1^2) + E_1(1-\nu_2^2)} \qquad (3.4)$$

Where, R, R_1, and R_2: effective radius, radius of the top and the bottom ball respectively.

E′, E_1, and E_2 : effective young's modulus, and young's modulus of the top and bottom ball, respectively.

ν_1 and ν_2 : poisons ratio of top and bottom ball respectively.

For four-ball tester, each lower balls experience the load and maximum contact pressure as 16.313 kgf and 3.402 GPa respectively.

The film thickness calculated using Eq. 3.5 and 3.6, by considering hard elastohydrodynamic lubrication condition (Hamrock et al., 2004):

$$\frac{h_{min}}{R_x} = 3.63\ U^{0.68}\ G^{0.49}\ W^{-0.073}(1 - e^{-0.68k}) \tag{3.5}$$

$$\frac{h_{min}}{R_x} = 3.63\ [\frac{v\eta_0}{E'R_x}]^{0.68}\ [\xi E']^{0.49}\ [\frac{w}{E'R_x^2}]^{-0.073}(1 - e^{-0.68k}) \tag{3.6}$$

Where, h_{min}: film thickness;

U, G and W: dimensionless speed, material and load parameter, respectively;

k: ellipticity parameter ;

R_x: effective radii in x-direction (i.e. $\frac{1}{R_x} = \frac{1}{R_{ax}} + \frac{1}{R_{bx}}$) ;

ν: top ball speed; η_0 : dynamic viscosity of oil (castor oil 0.28 PaS);

E': effective young's modulus; w: load

ξ: pressure-viscosity coefficient [$\xi = (0.6+0.965\log_{10} \eta_0) \times 10^{-8}$];

The film thickness was calculated by using Eq. 3.6 and found that it was less than 0.1µm. Therefore, this indicates that the system was in boundary lubrication regime. The detailed calculations are presented in the Appendix-A.

- ***Calculations of mean wear volume (MWV) of worn specimens for four-ball tester***

The MWV calculated with Equation (3.7). Equations (3.8) - (3.10) are the supporting relationship to calculate MWV.

$$MWV = \frac{\Pi d_0^4}{64r}\,[({}^{d}/_{d_0})^4 - ({}^{d}/_{d_0})] \quad (3.7)$$

Where, Mean WSD $d = (d_1 + d_2 + d_3)/3$ (3.8)

Hertzian diameter $d_0 = 2(\frac{3Pr}{4E'})^{1/3}$ (3.9)

Reduced radius $r = \frac{r_1 r_2}{r_1 + r_2}$ (3.10)

r_1, r_2, ν_1, ν_2 and E_1, E_2: radius, Poisson's ratio and Young's modulus of top and bottom balls.

- ***Calculations of specific wear rate for worn specimens***

Specific wear rate calculated with the help of Archard's equation (equation 3.11);

$$Specific\ wear\ rate = \frac{wear\ volume}{load * sliding\ distance} \quad (3.11)$$

3.3. The significance of the tribological test of the lubricants

Antiwear test

The antiwear test is performed to evaluate the material loss/wear resistant performance of the specific lubricant under the specified operating conditions. In four-ball tester, the material loss measured by the mean WSD of the three lower stationary balls. Larger WSD indicates higher material loss and poor performance of the lubricant and vice-versa.

Antifriction test

The antifriction test evaluates the potential of lubricant to reduce the friction which may cause by locking of the asperities and their collision when the mating surfaces in relative motion. The factors like tribo-film thickness, separation of asperity-asperity contact, etc. influence the capacity of the lubricant in this test.

Extreme-pressure (EP) test

The EP test provides the load carrying capacity of the lubricant. The duration of this test is 10 seconds. This test gives an insight of the lubricant capacity under higher loads. As per the Table 3.5, the load increased gradually in each test until welding of all four balls occurs. If the test rig runs till end of the test then it is known as pass load (or last non-seizure load). However, if test rig stops in between and all four balls welded together, then it is known as weld load capacity of the lubricant. For next higher loads it is mandatory to prepare the fresh sample.

3.4. Characterization of the samples

Different analytical tools have been used in the present work to investigate the nanoparticles parameter like size, shape, worn surface analysis, confirmation for oil modification, etc. The detailed instruction and operating parameters of the characterization instruments have discussed as follows:

3.4.1. Scanning electron microscope (SEM) and Energy dispersive spectroscopy (EDS)

SEM was used to record the morphology of the object surface with the help of SEM-Zeiss EVO 18 Research, Germany as shown in Figure 3.3. The operating voltage was kept constant at 20kV. The worn surfaces and nanoparticles examined at various magnifications. The worn surfaces analyzed by EDS, equipped with SEM, for elemental analysis or chemical characterization of a sample. Since each element has some distinct specific energy, therefore on the basis of that specific energy the element was identified. An EDS measures X-ray counts (on Y-axis) and energy emitted (on X-axis) from a test sample.

3.4.2. Transmission electron microscope (TEM)

The size and shape of the synthesized CCTO nanoparticles recorded with the help of TEM-FEI Technai F20 S/TEM, (United States) is shown in Figure 3.4. The operating voltage was kept constant at 200 kV, while a high vacuum in the range of 10^{-6} Torr was maintained for characterization. A very small amount of nanoparticles have dispersed in acetone for sample preparation, then one drop of solution put on the TEM grid (copper material, 3 mm diameter, 100μm thick). Thereafter, grid kept in a hot environment to evaporate acetone as well as any moisture content. In this way, the moisture-free particles entrapped in the mesh, used for the further evaluation.

3.4.3. X-ray diffractometer (XRD)

Phase identification of the sample was performed by using Rigaku Ultima IV X-ray diffractometer, Japan as shown in Figure 3.5. XRD is an X-ray imaging technique which works on the principle of Bragg diffraction. The confirmation of synthesized CCTO particles was done at a diffraction angle (2θ) ranging from 10° to 80° (Cu-K_α radiation). The intensity of the X-ray beam diffracted from the sample provides diffraction topography. The distribution of the scattering from the sample reflects the intensity mapping.

Figure 3.3. SEM set-up.

Figure 3.4. TEM set-up.

3.4.4. Atomic force microscope (AFM)

The surface roughness (2-dimensional and 3-dimensional) of the worn surfaces measured by using the AFM model BT 02218, Nanosurf easyscan 2 basic AFM, Switzerland as depicted in Figure 3.6. The AFM used in contact mode with silicon cantilever having Au high reflecting coating. The scanning tip was mounted at the free end of a cantilever. Firstly, the worn surface was cleaned with acetone, thereafter roughness of the worn track was recorded for the area of 50 µm x 50 µm and 70µm x 70µm. And, the line roughness was measured across the worn track. In few cases scanning probe microscope (SPM) was also used to measure the roughness. SPM is also a specially configured AFM.

3.4.5. Fourier transform infrared (FTIR) spectroscopy

FTIR is a potential analytical tool to identify unknown materials as well as assess the quality of a sample. Since each material has distinct arrangement of the atoms therefore unique spectrum produces for every material. In the present study, FTIR spectroscopy of the prepared sample observed between 4000–500 cm^{-1} wavenumber with Bruker Alpha Eco-ATR, Germany and depicted in Figure 3.7. It was used to analyze the surface treatment of the nanoparticles and confirmation of oil modification. The spectrometer furnished with *Zinc selenide (*ZnSe) crystal. Numbers of scans used were 25.

3.4.6. Nuclear magnetic resonance (NMR) spectroscopy

Quantitative ^1H NMR spectra obtained with a Bruker 500 AVANCE III HD spectrometer (Bruker, Rheinstetten, Germany) at 500 MHz frequency using a 5mm dual probe (Figure 3.8). The test sample was prepared in $CDCl_3$ (99.8% deuterated chloroform). This is because $CDCl_3$ is non-reactive and not participates in exchange of its deuterium with oil molecule protons. 16 repeated scans were performed to obtain NMR spectra. The peak assignments were made using zg30 and zgpg30 pulse sequence.

3.4.7. Gas chromatography mass spectroscopy (GC-MS)

GC-MS is an analytical tool which contains the feature of both gas-chromatography (GC) and mass spectrometer (MS). It was used to measure the different contents present within the test sample. In this study, the prepared oil sample (by esterification to form volatile fatty acid methyl ester of oil) injected through the heated inlet port (to vaporize) and moved with inert carrier gas helium. GC separates the components in the sample and MS gives detailed structural information. The instrument GC/MSD 5975C, Agilent Technologies, U.S.A. was used in this study (Figure 3.9). Operating condition for GC injection parameter was splitless mode at temperature 380°C, purge flow 50 ml-min^{-1}, pressure 98.6 kPa; column parameter: constant flow, maximum temperature 400°C, average velocity 46 cm/s, and outlet as MS (with electron ionization, magnetic field, and detector). MassHunter software used for the data analysis.

3.4.8. Thermogravimetric analysis (TGA)

TGA is an analytical tool used to observe the weight loss or gain of the material. This change in weight is correlated as the function of temperature or time. In the present study change in the lubricant weight measured with TGA-1, Mettler Toledo, Greifensee, Switzerland (Figure 3.10). Thermo-oxidative stability of the base oils was studied under air environment (20 mL/min). The sample mass was 8 mg (approx.) placed in the sample pan placed over a precision thermo-balance inside the furnace. The heating rate was kept 10°C/min up to 750°C. The thermo-oxidative stability of the oil sample observed as the function of initial decomposition temperature (T_{onset}). When the curve plotted for weight loss in percentage (at Y-axis) against temperature (at x-axis), a sudden drop in the progressive curve can easily be observed.


Figure 3.5. XRD set-up.


Figure 3.6. AFM set-up.


Figure 3.7. FTIR set-up

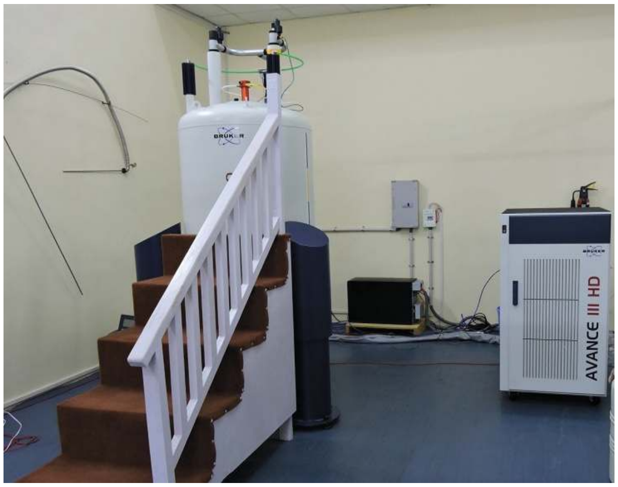
Figure 3.8. NMR set-up.


Figure 3.9. GC-MS set-up.

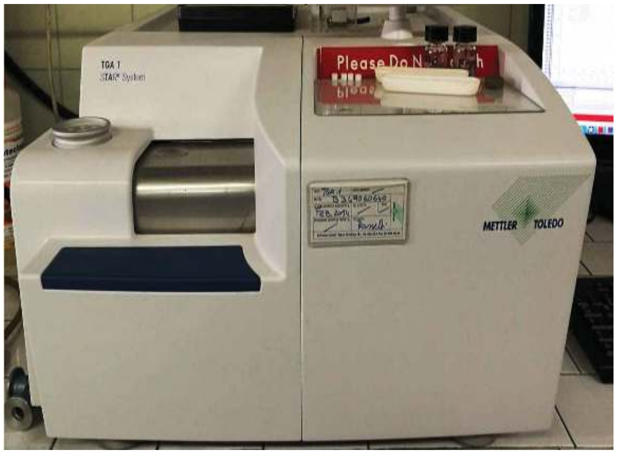
Figure 3.10. TGA set-up.

The perfect tangents require drawing through the horizontal and vertical/inclined portion of the obtained GC-MS curve. Intersect of these two tangent lines provides the decomposition temperature.

3.5. Other instruments involved in experimentation

3.5.1. Magnetic stirrer cum hot plate

In the present work, the solution was agitated with magnetic stirrer cum hot plate instrument (model IKA, C-MAG, HS4 Digital, Germany). A heating element is coupled with the stirrer to heat the sample up to the 500°C temperature. In the conditions like epoxidation where the constant temperature was mandatory, a thermocouple used (attached to the stirrer cum hot plate) to measure the exact temperature of the solution. By this device stirring and heating, both can be done simultaneously or individually depending upon the requirement.

3.5.2. Ultrasonicator

Ultrasonicator is used to provide the ultrasonic pulse wave to the nanoparticles in the oil so that it can be in suspended condition for an extended period without agglomeration. The maximum attaining temperature was 80°C and frequency 40 kHz.

3.6. Summary of the chapter

This chapter provides an insight to the used approach for sample preparation and tribo-testing, the basic calculations for tribological parameters and brief introduction of all the analytical tools used in the present work.