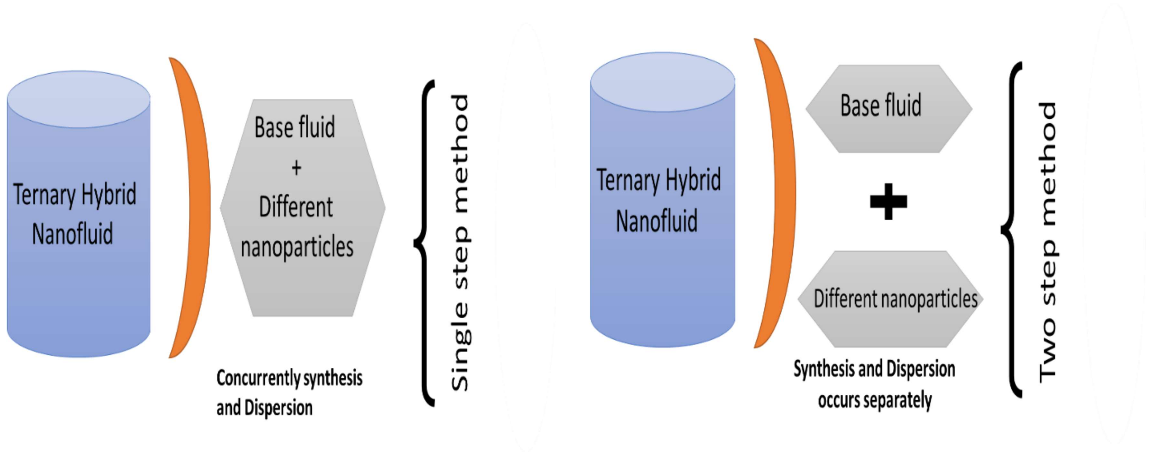
Chapter 3

Preparation and Characterization

The present chapter includes the preparation of hybrid nanofluid, characterization of nanoparticles, stability of THNF, and its characterization with their thermophysical properties evaluation.

3.1 Preparation of hybrid nanofluids

Two step method and single step method are the two different techniques by which hybrid nanofluid can be prepared. As, nanoparticles agglomeration with its instability issue in the case of single step method, two step method is widely used for the preparation of hybrid nanofluid (**Raja et al., 2016, Hayat et al., 2017, Gupta et al., 2018, Sajid et al., 2018, and Shah et al., 2019**). A simple layout chart for the preparation of hybrid nanofluid using the two different techniques is depicted in the Fig. 3.1. In single step, nanoparticles are manufactured and concurrently disseminated into the base fluid to prepare nanofluid. In contrast, a two-step method involves the production of nanoparticles by chemical or mechanical process and then disperse into the required base fluid. As, due to poor dispersion, the thermal conductivity of the hybrid nanofluid may get vary. To significantly improve the properties of hybrid nanofluids, many



(a) (b)

Fig. 3.1. Synthesis of Ternary hybrid nanofluid, (a) Sigle step; (b) Two step method.

strategies are applied to obtain a suitable suspension of nanoparticles in the base fluid. For the preparation of hybrid nanofluid, three different nanoparticles are disseminated into base fluid and thus called Ternary Hybrid nanofluid (THNF) preparation at three different concentrations. For comparison, two different nanoparticles are mixed into the base fluid at a fixed 0.12%(v/v) volume concentration to prepare another hybrid nanofluid. In the research work, water is taken as the base fluid in which nanoparticles are dispersed.

Three different oxides of nanoparticles (Al_2O_3, CuO, and TiO_2) have been used in the present investigation. The copper oxides (CuO) and aluminum oxides (Al_2O_3) nanoparticles are commercially procured from Alfa Aesar, USA of average size 30 - 50nm diameter while TiO_2 nanoparticles are procured from Sisco Laboratories private limited, India with average particle sizes in the range of 32 - 50nm. The thermal and physical properties of the procured nanoparticles are listed in Table 3.1. In this study, three different THNF solution is prepared of 0.06, 0.09, and 0.12% volume concentration. The three different solid nanoparticles are dispersed into the base fluid, the water of equal vol/vol ratio. As the presence of dissimilar nanoparticles reduces the attractive forces and prolongs the dispersion. For the hybrid nanofluid, three different nanoparticles are selected. Low concentration has been chosen for the present study mainly due to two reasons; (a) low concentration results lower number of nanoparticles and thus prolongs the stability, and (b) Chances of clogging would be less due to intrusive geometry.

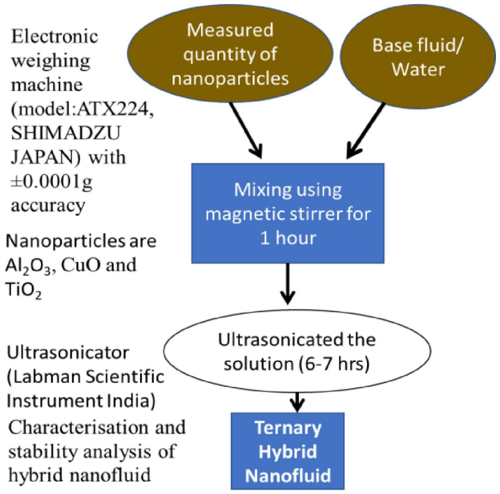


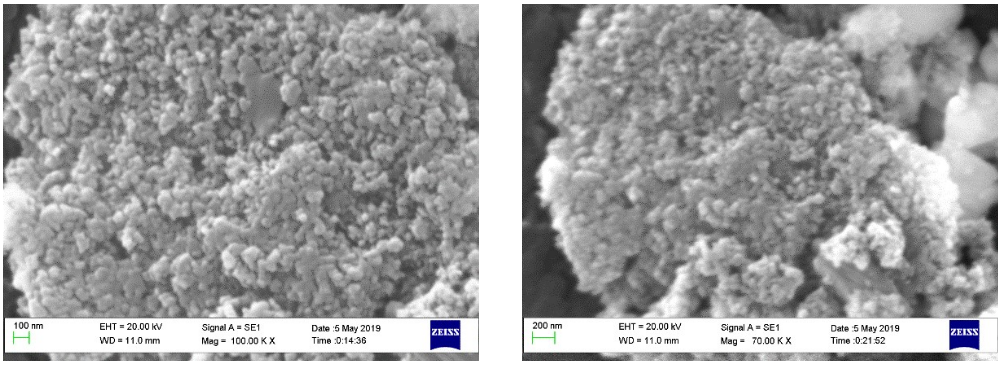
Fig. 3.2. Two step method layouts of the present investigation.

In the present investigation, Ternary hybrid nanofluid is prepared using the two-step method. The process layout procedure of the two-step method has been presented in the Fig. 3.2. Hybrid three different nanoparticles, at a particular volume concentration, the volume of the nanoparticles are fixed and thus the mass of the respective nanoparticles is calculated and weighed using an electronic weighing machine of model ATX224, SHIMADZU, JAPAN with an accuracy of ±0.0001g and then dispersed into the base fluid water.

Once the nanoparticles are measured, the homogeneous dispersion of nanoparticles into the base fluid is the primary objective. Therefore, using a magnetic stirrer hot plate device consisting of an inbuilt speed controller (Manufacturer: SSILAB, 600W, 1200RPM), the solution is stirred for an hour. Then, the second nanoparticles are added and stirred for an hour followed by the third nanoparticles and stirred for another hour. After then, for proper disruption of the nanoparticles to the base fluid, the solution is further sonicated for 6 - 7hours at a fixed temperature (40°C) using an Ultrasonicator device of specification (Labman Scientific Instruments, India, 40kHz.) to ensure the homogeneity of the mixture. Through the same procedure, the three different concentration of a homogeneous solution is prepared.

3.2 Characterization of the nanoparticles

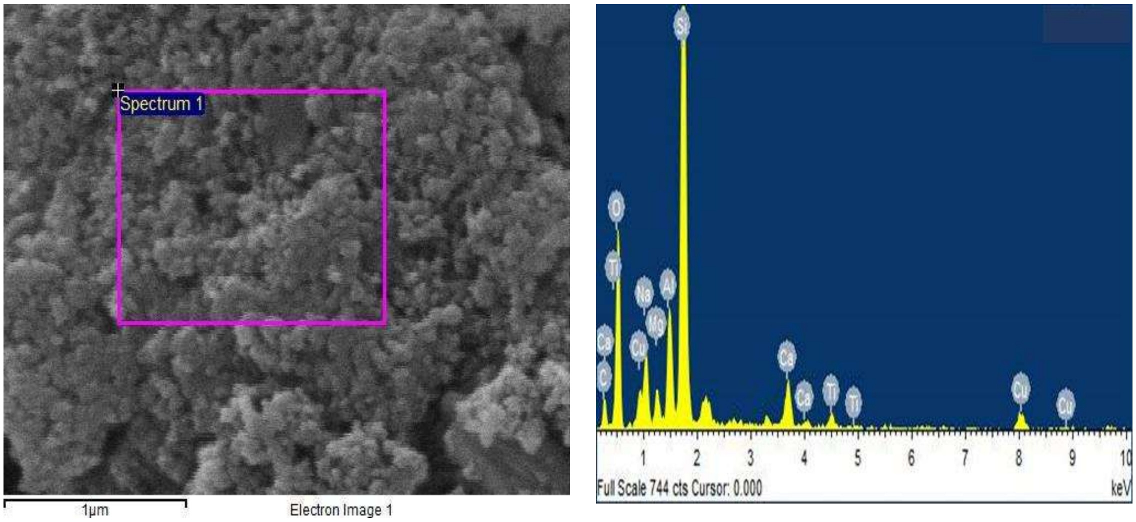
The structure, morphology, nanoparticles, and distribution has been investigated using SEM (Scanning electron microscopy) at different magnification and sizes for a 0.12% (v/v) sample of the THNF. For the preparation of the SEM analysis, the sample is collected, kept on the glass slide, and allowed the water to evaporate. Once the water evaporates from the glass slide, then the glass slide sample has been used for SEM analysis for the morphology investigation and the EDX (Energy Dispersive X-Ray) for the nanoparticle elemental investigation. Spherical morphology is investigated with a nearly stable solution, and particle distribution is uniformly decorated and well spread. Surface regularity is represented in the Fig. 3.3.(a) from THNF with a noticeable spherical shape also shown in the Fig. 3.3.(b). The image showed well and thoroughly spread nanoparticles which indicates a stable solution while the morphology is visible as spherical. Fig 3.3, (a)100k and (b) 70k magnification showed a homogenous spread of nanoparticles while the shape is spherical. SEM illustrated a stable chemical composition of nanoparticles and also found them compatible with one another. A low quantity was chosen for nanoparticles due to the nice combination and feasible dispersion in the solution prepared.



(a) (b)

Fig. 3.3. SEM morphology of 0.12% volume fraction THNF nanoparticles at different sizes and magnification, (a) 100nm, 100.00 K X mag.; (b) 200nm, 70.00 K X mag.

However, the visual image depicts and shows a denser nanoparticle distribution with some patches. Those structures with patches overlapping interpret with one another. The crucial differentiation of small, unlike residue, covers the entire nanofluid surface with a high-density region at lower magnification. The particle's chemical composition found stable with the other nanoparticles, and few agglomerated nanoparticles found compatible with one another. Of the prepared solution, EDX (Energy-dispersive X-Ray) analysis has been also examined to identify the elemental composition using the X-ray technique. The spectrum of the sample size shown in Fig. 3.4.(a) and their corresponding elements availability within the selected spectrum size of 1 μm depicted in Fig. 3.4.(b). The peak in the EDX analysis represents the presence of that element. It is clear from the EDX analysis that there is a presence of Aluminium (Al), Copper (Cu) and Titanium (Ti) could be used for the mapping of the elements. However, the presence of silicon (Si), Calcium (Ca), and Magnesium (Mg) elements is also identified due to the presence of elements in the water. Therefore, a correct elemental mapping of the prepared sample was achieved successfully through EDX analysis.

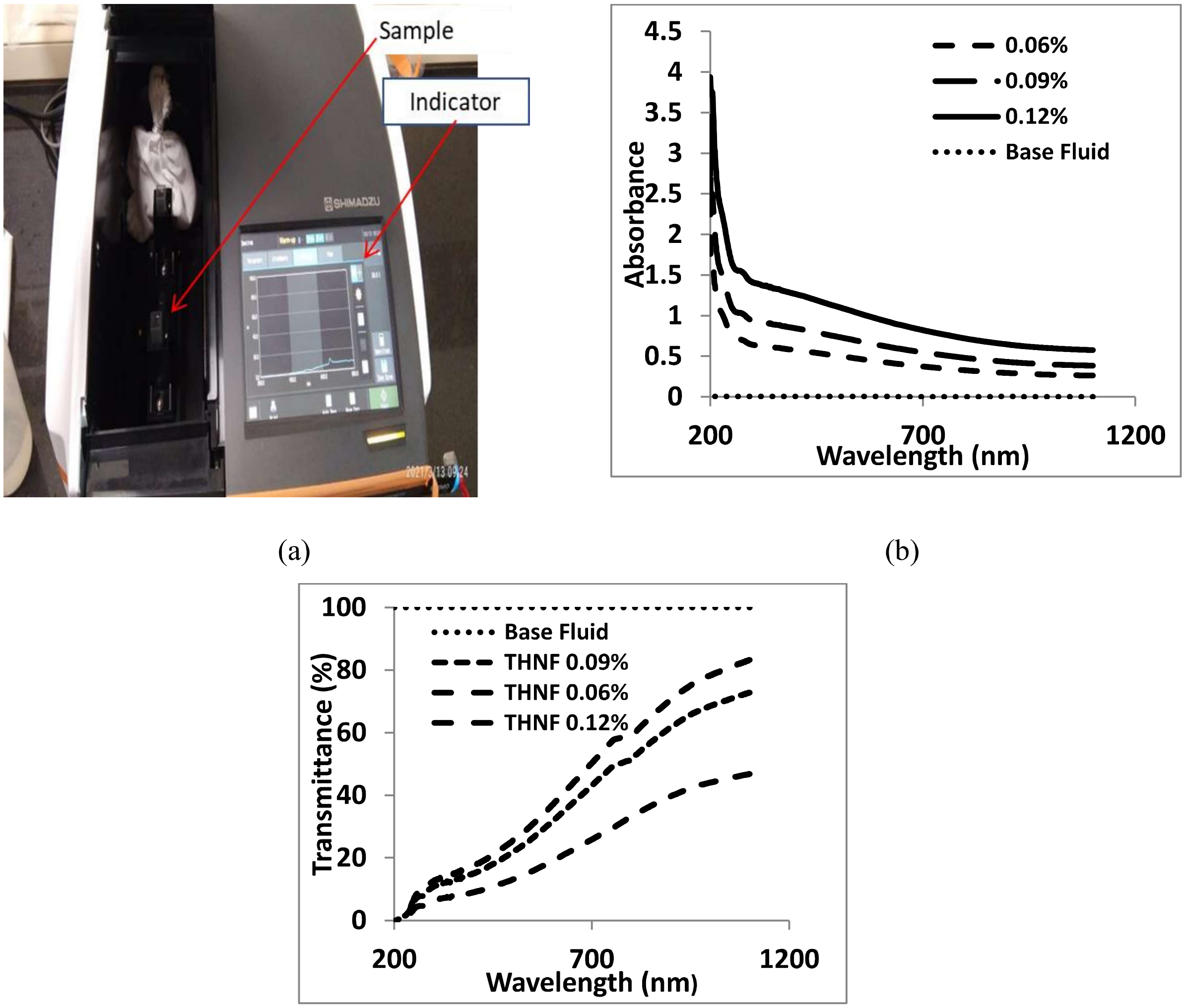


(a) (b)

Fig. 3.4. EDX image of the Ternary hybrid nanofluid, (a) Spectrum from a sample size of 1μm magnification; (b) Element availability within spectrum size.

3.3 Characterization of the THNF's

Characterization of ternary hybrid nanofluids is important for the purpose to utilize the solution for practical heat transfer applications. Thermal, rheology, and pH characterization has been considered in the present study for the THNF's. Homogeneous dispersion and stability analysis has been discussed in the present section and the thermal, and physical characteristics are discussed in the later section 3.5.



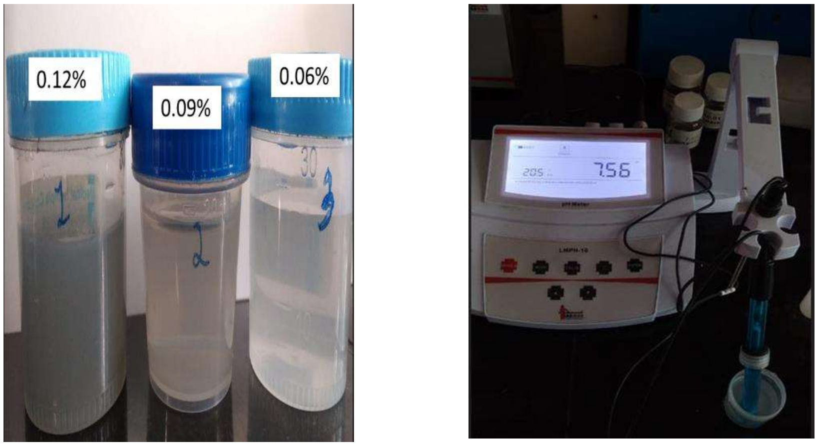
(a) (b)

(c)

Fig. 3.5. Dispersion analysis, (a) Ultraviolet visible Spectrophotometer with sample; (b) Absorbance of THNF at a different wavelength and concentrations; (c) Transmittance spectra of THNF at a different wavelength and concentrations.

THNF stable dispersion is analyzed using an ultraviolet visible spectrophotometer (Shimadzu, Uv1900) on measuring absorbance, and transmittance of the sample as shown in Fig. 3.5.(a). The 10ml sample is collected in the quartz lid sample collector cuvette and set the wavelength from 200nm-1100nm, the digital display shows the variation plot, and results are collected. The spectrophotometer test is first run for the base fluid water and then the rest of the samples of THNF was used for the absorbance and transmittance analysis. Fig. 3.5.(b) shows the absorbance of nanofluids for a 200-1100nm range of wavelength. Absorbance indicates the wave energy that is lost when traveling through the THNF. Higher concentration results in higher absorption which leads to a better-suspended nanofluid. For base fluid, absorbance is nearly zero, and nanoparticle addition causes an increment in absorbance. However, from 200 to 800nm absorbance decreases exponentially and beyond that, no sufficient change is admired. A larger presence of nanoparticles causes larger scattering and absorbs optical light of a certain wavelength therefore a well-distributed nanoparticle suspension into the base fluid was achieved successfully. Also, Fig. 3.5.(c) shows the transmittance of the THNF at different volume fractions in a range of 200-1100nm wavelength measured using a spectrophotometer. For base fluid, the transmittance is nearly 100% and nanoparticle addition causes a decrement in transmittance. Among the THNF samples, 0.06% concentration of THNF shows the highest transmittance while 0.12% THNF shows the lowest transmittance. The presence of a high number of nanoparticles at higher concentrations, due to little agglomeration and well dispersion of nanoparticles enables the light to strike on the particle and get scattered within and thus shows the lowest transmittance.

Also, the stability of the prepared THNF solution is analyzed using the concept of isoelectric point (IEP). This method reveals if the solution pH is aways from the IEP, the nanofluid remains stable with no sedimentation. However, this method is mostly suitable for lower concentrations. In the present study lower concentration (0.06-0.12%) of the THNF is prepared and characterization is studied. To ensure a stable hybrid nanofluid, the pH must be away from the IEP, to have a larger repulsive force for the well-separated and dispersed nanoparticles. The IEP of three nanoparticles, used for the preparation in the present study is listed in the Table 3.1. The higher concentration of the nanoparticles, when the pH value reaches the IEP, then the net charge of the particles is zero, and settling of the nanoparticles occurs. Thus, a lower concentration is prepared (0.06-0.12%). For measurement of the pH of the prepared solution, the solution is collected as shown in the Fig. 3.6.(a), and pH is measured using the pH measurement device (LABMAN model) as shown in the Fig. 3.6.(b). The pH of the different working fluids measured is listed in the Table 3.2. The measured pH value of the working fluid obtained away from the IEP of the respective nanoparticles ensures the working fluid is stable and no sedimentation of the nanoparticles occurs and could be used for practical applications. Moreover, for the assurance of the homogeneous dispersion of the nanoparticles, the pH, density, and viscosity of the prepared THNF were determined for the different samples collected from random positions and obtained no change in the parameters measured all at room temperature.



(a) (b)

Fig. 3.6. (a) Samples collected for the characterization of THNF at different concentrations; (b) pH measurement device.

3.4 Thermophysical properties of the working fluids.

To utilize the nanofluid for thermal applications, the thermophysical properties of the working fluid information are required. The hybrid nanofluid is stable, nanoparticles are well dispersed into the base fluid. In the present study, the thermophysical properties of the working fluids are measured experimentally with the help of suitable devices.

3.4.1 Measurement procedure

To measure the properties of the working fluids (THNF and water) different devices like Hot disk TPS 500 thermal constant analyzer for measurement of thermal conductivity and specific heat, DV1 Brookfield viscometer (plate and cone) for viscosity measurement and electronic weighing machine to measure density have been used. For the density (ρ) measurement of the working fluids, $\rho = m/v$ has been used, where m is mass in kg and v is the volume of the working fluid in m^3. For the density, a scaled beaker is used and weighted using the electronic weighing machine (model: ATX224, SHIMADZU, JAPAN) as presented in Fig. 3.7.(a). Then a specified sample of the working fluid was taken and kept in the marked beaker to measure the weight. Once the total mass is obtained, the mass of the weighted beaker is subtracted, and obtained the net mass of the sample fluid. Then the net mass of the sample fluid is divided by the sample volume gives the density of the fluid. To measure the viscosity of the working fluids, DV1 Brookfield Viscometer of cone and plate type was used as shown in the Fig. 3.7.(b). The operating principle of this viscometer: a calibrated spring spindle is connected to the plate which is submerged into the sample fluid and as the plate rotates, due to fluid viscous drag, the spring deviates and the deflection of the spring shows the viscosity of the fluid on the display. For low viscous fluids, the larger surface area of spindles and higher rotational speeds and vice versa if for thick fluids. The minimum sample of fluid for the measurement of the viscosity is 1.0ml and CP-42 spindles were used for the viscosity measurement. Working fluids, water, and THNF of low concentration (0.06-

0.12%) have been used in the present investigation. At such low concentrations of the THNF, linear variation in shear stress and shear strain rate ensures the applicability of the Newtonian fluid. (**Luo et al., 2014; Senthilraja et al., 2015, Valan et al., 2019.**)

To measure the thermal conductivity and specific heat of the working fluids, a thermal constant analyzer was used as shown in Fig. 3.7.(c) with their component details which work on the principle of transient plane source method. In between the Kapton polyimide film, the nickel foil sensors were embedded and a double spiral wounding of radius 3.19mm. When the device is on, a spherical wave is generated at one end of the probe and travels to the sample using a heating power source. Under constant heating rate, hot disks measure the sample thermal conductivity and thermal resistivity from the increment in probe temperature. This set up can measure the thermal conductivity in the range of 0.2 - 2W/mK with an accuracy of ±2%. The hot disk thermal analyzer directly gives the volumetric heat capacity (ρc_p) and specific heat capacity of working is determined by dividing it by the measured density of the sample.

(a) (b) (c)

Fig. 3.7. Photographs of, (a) Electronic weighing machine; (b) DV1 Brookfield Viscometer; (c) Hot disk thermal constant analyzer.

3.4.2 Results and discussion

Different nanoparticles used in the present investigation with their thermophysical properties are listed in Table 3.1. Commercial water is used as the base fluid in the entire study. The density of the aluminium oxide nanoparticles is the lowest and the highest density is for the copper oxide nanoparticles. The density of the titanium oxide nanoparticles is medium compared to other selected nanoparticles. Also, the particle size and isoelectric point of the nanoparticles studied are listed in Table 3.1.

Table. 3.1 Thermal and physical properties of the procured nanoparticles.

Particles	**Aluminium Oxide (Al_2O_3)**	**Titanium Oxide (TiO_2)**	**Copper Oxide (CuO)**
Density(kg/m^3)	3890	4170	6310
Specific heat (J/kg.K)	880	711	531
Thermal conductivity (W/mK)	40	4.8	48
Particle Size (nm)	32	40	50
Colour	White	White	Black
Isoelectric point (IEP)	9.1 (**Singh et al., 2005**)	10.5 (**Hetlani et al., 2017**)	10 (**Sousa and Teixeira 2013**)

The density of the colloidal mixture THNF, relies upon base fluid and nanoparticle densities. On the addition of nanoparticles into the base fluid, solid particles exhibit higher density comparatively. Therefore, the mixture density increased. The density of nanofluid plays a crucial role in affecting the performance parameter of a device. As the nanoparticles are added into the base fluid water, from low concentration to a little higher concentration, the density of the THNF increases.

Table. 3.2 Thermophysical properties of different working fluids

Working fluids	**Density (kg/m^3)**	**Dynamic viscosity (Pa.s)**	**Thermal conductivity (W/m-K)**	**Specific heat (J/kg.K)**	**pH value**
Water	988	0.00066	0.630	4181.24	6.97
Al_2O_3+TiO_2+CuO/ Water (0.06%)	998	0.00072	0.643	4173.32	7.56
Al_2O_3+TiO_2+CuO/ Water (0.09%)	1010	0.00077	0.650	4167.51	7.78
Al_2O_3+TiO_2+CuO/ Water (0.12%)	1025	0.00084	0.661	4162.42	8.02
CuO +TiO_2 / Water (0.12%)	1028	0.00079	0.649	4082.35	8.21
Al_2O_3+TiO_2/ Water (0.12%)	1015	0.00070	0.638	4171.61	8.16

The thermal conductivity of the hybrid nanofluid (0.06-0.12% v/v) is higher than the base fluid water thermal conductivity. On the addition of nanoparticles, due to the higher thermal conductivity of the nanoparticles, the thermal conductivity of the THNF is also higher.

The increment in thermal conductivity on nanoparticle addition into the mixture could be due to Brownian motion, which influences the nanoparticle behavior in the base fluid. Results revealed that thermal conductivity improves with volume concentration increment due to the combined effect of solid particle motion and rapid intercollision between the water molecule and solid particles. THNF at 0.12% (v/v) concentrations shows 2.9% higher thermal conductivity compared to the lowest 0.06% (v/v) concentration and 5% higher than the base fluid. Also, the hybrid nanofluid, CuO +TiO_2 / Water, and Al_2O_3+TiO_2/ Water at 0.12% (v/v) concentration show relatively lower conductivity than THNF of 0.12% (v/v). This low thermal conductivity could be due to lesser repulsive force in presence of two different nanoparticles than in the presence of three different nanoparticles in the case of THNF. The above result can be back up with the pH measurement. The pH of THNF is slightly lower than the hybrid nanofluid. Furthermore, the details of the thermal conductivity, and pH of the different working fluid is listed in the Table 3.2.

For a fluid to be used for practical applications, the viscosity of the fluid plays a critical role. Viscosities of THNFs are obtained to be higher in contrast to the base fluid. With nanoparticle addition, the surface area increases and thus causes more friction between the solid surface and the fluid and enabling additional increment in the viscosity (**Abbasi et al., 2013; Sundar et al., 2014; Dardan et al., 2016**). The viscosity of THNF is higher than base fluid, and with nanoparticles addition, the density, thermal conductivity, and viscosity get increase, and the specific heat capacity decreases. THNF of 0.06% (v/v), combination shows 9.7% higher viscosity, and THNF of 0.12% (v/v) combination shows 27% higher viscosity compared to the base fluid water. Hybrid nanofluid of copper and titanium oxides with water base fluid shows 6.1% lower viscosity than the THNF of 0.12% (v/v) concentration. The specific heat capacity of the prepared stable solution was also measured. This property plays a crucial role and influences heat transfer performance. The addition of nanoparticles resulted in a decrement in specific heat capacity as solid particles display lower heat capacity than base fluid water, therefore prepared mixture obtains lower specific heat capacity.

Thermal conductivity, dynamic viscosity, specific heat capacity, and density of THNF at 0.12% (v/v), volume concentration is 0.661 W/mK, 0.00084 Pa.s, 4162.42 J/kgK, and 1025 kg/m^3.

3.5 Highlights

The present investigation focuses on the preparation and characterization of hybrid, and ternary hybrid nanofluids. The two-step method has been employed for the preparation of the mixture preparation. Then synthesized working fluids have been characterized (SEM and EDX) and their thermal and physical characteristics have been measured and tabulated. Also, the morphology of nanoparticle shape, nanoparticle sizes, and elemental mapping have been investigated using SEM and EDX. The stability of the THNF has been proven by the ultraviolet visible spectrophotometer and isoelectric point method. In the present study, several observations are as follows:

- All the nanoparticles are of the spherical shape of dimensional size and lie within lesser than 100nm. Elemental mapping ensures the presence of selected nanoparticles.
- Ultraviolet visible spectrophotometer and pH value method confirmed the nanofluid to be stable. And the stability gets lower with the rise in volume concentration of hybrid nanofluid. Minimum stability obtained for 0.12% (v/v) concentration of THNF solution and maximum stability obtained for 0.06% (v/v) concentration of THNF. The pH of the THNF solutions are away from the IEP, which confirms the solution to be stable to use for practical applications.
- The prepared colloidal solutions are dispersed homogeneously by measuring the prepared sample thermo-physical properties collected from the distinct locations.

- Measured parameters, thermal conductivity, density, and viscosity of the THNF's increase while specific heat capacity reduces with the rise in volume concentration from 0.06-0.12%.
- The pH value of the THNF is increased with the rise in concentration from 0.06%-0.12%(v/v). For hybrid nanofluid at the same concentration 0.12%(v/v), is highest 8.21.

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