Sudan University of Science and Technology

College of Graduates Studies

Synthesis, Characterization and Determination of the Thermophysical Properties of Copper (II) Oxide/water Nanofluid

تخليق وتشخيص وتقدير الخواص الفيزيوحرارية للمائع النانوي لأوكسيد النحاس(II)

A Thesis Submitted in Partial Fulfillment for the Requirement of the Degree of M.Sc. in Chemistry

By

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إستهلال

بسم الله الرحمن الرحيم

قال تعالـــــى:

وَقُل رَّبِّ زِدْنِي عِلْمًا

(سورة طه : 114)

صدق الله العظيـــم

أ

Dedication

To my

    parents,

        husband,

            brother and sisters

Acknowledgement

All praise is due to Allah The Most Gracious The Most Merciful for giving me the strength and patience to accomplish this work.

I would like to express my appreciation to my supervisor Dr. Mohammed Suleiman Ali Altoum for his continuous encouragement and support.

I extend my thanks to everybody who helped me to finish this project.

Abstract

Copper (II) oxide /water nanofluid was prepared in two steps by using wet chemical method to prepare copper oxide nanoparticles and ultrasonic vibration for dispersing nanoparticles into de-ionized water. The characterization results show that the preparing of copper oxide /water nanofluid was successful.

The thermophysical properties: density, viscosity, Specific heat capacity and thermal conductivity were studied at different concentrations of the nanofluid (1, 2, 3 and 5) Wt%. The measuring results of the thermophysical properties show that at constant temperature; density, viscosity and thermal conductivity were found to increase by increasing the concentration of nanofluids. But the specific heat of nanofluid decreases with the increase in concentration.

The stability of the nanofluid was measured and it found that nanofluids are stable for approximately 25 days.

المستخلص

تم تحضير المائع النانوي لأوكسيد النحاس(II) في الماء في مرحلتين باستخدام طريقة wet chemical لتحضيربدرة نانو اوكسيد النحاس و ultrasonic vibration لتوزيع جزيئات النانو داخل الماء منزوع الايونات. النتائج التشخيصية اظهرت ان التحضيرللمائع النانوي لأوكسيد النحاس في ماء منزوع الايونات كان ناجحا .

الخواص الفيزيوحرارية : الكثافة ، اللزوجة ، سعة الحرارة النوعية والتوصيل الحراري تم قياسها ودراستها لتراكيز مختلفة من المائع النانوي (1 ,2, 3 ,5) % Wt. النتائج المقاسة للخواص الفيزيوحرارية اظهرت انه عند درجة حرارة ثابتة ؛ الكثافة واللزوجة والتوصيل الحراري تزيد بزيادة تركيز المائع النانوي. بينما السعة الحرارية للمائع النانوي تقل مع زيادة التركيز.

الاستقرارية للمائع النانوي تم قياسها ، ووجد انه مستقر لمدة 25 يوم.

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Introduction and Literature Review

Chapter One

1. INTRODUCTION

1.1. Important Nomenclatures:

1.1.1. Nanoparticles are particles between 1 and 100 nanometres (nm) in size with a surrounding interfacial layer [1].

1.1.2. A substance in liquid / gas phase is referred as '**fluid**'. Distinction between a solid and a fluid is made on the basis of substance's ability to resist an applied shear (tangential) stress that tends to change its shape.

Ultrahigh-performance cooling is one of the most vital needs of many industrial technologies. However, inherently low thermal conductivity is a primary limitation in developing energy-efficient heat transfer fluids that are required for ultrahigh-performance cooling. Modern nanotechnology can produce metallic or nonmetallic particles of nanometer dimensions.

Nanomaterials have unique mechanical, optical, electrical, magnetic, and thermal properties [2].

1.1.3. Nanofluids are engineered by suspending nanoparticles with average sizes below 100 nm in traditional heat transfer fluids such as water, oil, and ethylene glycol. A very small amount of nanoparticles, when dispersed uniformly and suspended stably in fluids, can provide dramatic improvements in the thermal properties of fluids.

Nanofluids (nanoparticle fluid suspensions) is the term coined by Choi (1995) to describe this new class of nanotechnology-based heat transfer fluids that exhibit thermal properties superior to those of their host fluids or conventional particle fluid suspensions [2].

Nanofluid technology, a new interdisciplinary field of great importance where nanoscience, nanotechnology, and thermal engineering meet, has developed largely over the past decade. The goal of nanofluids is to achieve the highest possible thermal properties at the smallest possible concentrations (preferably<1% by volume) by uniform dispersion and stable suspension of nanoparticles (preferably<10 nm) in host fluids. To achieve this goal it is vital to understand how nanoparticles enhance energy transport in liquids [2].

Nanofluids are being developed to achieve ultrahigh-performance cooling and have the potential to be next-generation coolants, thus representing a very significant and far-reaching cooling technology for cross-cutting applications.

The conventional way to enhance heat transfer in thermal systems is to increase the heat transfer surface area of cooling devices and the flow velocity or to disperse solid particles in heat transfer fluids. However a new approach to enhancing heat transfer to meet the cooling challenge is necessary because of the increasing need for more efficient heat transfer fluids in many industries, such as the electronics, photonics, transportation, and energy supply industries [2].

1.2. Importance of Nanosize:

Solid particles are added because they conduct heat much better than do liquids. The major problem with the use of large particles is the rapid settling of these particles in fluids. Other problems are abrasion and clogging. These problems are highly undesirable for many practical cooling applications. Nanofluids have pioneered in overcoming these problems by stably suspending in fluids nanometer-sized particles instead of millimeter- or micrometer-sized particles.

Compared with microparticles, nanoparticles stay suspended much longer and possess a much higher surface area. The surface/volume ratio of nanoparticles is 1000 times larger than that of microparticles. The high surface area of nanoparticles enhances the heat conduction of nanofluids since heat transfer occurs on the surface of the particle.

The number of atoms present on the surface of nanoparticles, as opposed to the interior, is very large. Therefore, these unique properties of nanoparticles can be exploited to develop nanofluids with an unprecedented combination of the two features most highly desired for heat transfer systems: extreme stability and ultrahigh thermal conductivity. Furthermore, because nanoparticles are so small, they may reduce erosion and clogging dramatically. Other benefits envisioned for nanofluids include decreased demand for pumping power, reduced inventory of heat transfer fluid, and significant energy savings [2].

Table (1.1): Comparison of the old and the new materials.

	Microparticles	Nanoparticles
Stability	Settle	Stable (remain in suspension almost indefinitely)
Surface/volume ratio	1	1000 times larger than that of microparticles
Conductivity [a]	Low	High
Clog in microchannel?	Yes	No
Erosion?	Yes	No
Pumping power	Large	Small
Nanoscale phenomena?	No	Yes

* [a]: At the same volume fraction [2].

1.3. Advantages of nanofluids:

Particle size is the major physical parameter in nanofluids, since it can be used to attune the nanofluid thermal properties as well as the suspension stability of nanoparticles. Hence, nanofluids can able to flow freely through mini or micro channels with the dispersion of nanoparticles. The nanosuspensions show high thermal conductivity which is mainly due to enhanced convection between the nanoparticles and base liquid surfaces.

Another potential benefit is that the nanoparticles have lower dimensions so that the dispersed nanoparticle seems to be like a base fluid molecule in suspension.

The advantages of suspending nanoparticles in base fluids:

• The surface area and heat capacity of the fluid are increased.

• The effective thermal conductivity of the fluid is enhanced.

• The collision and interaction among particles, the surface of flow passage and base fluids are intensified.

• Reduction of particle clogging rather than conventional slurries.
The combination of these factors makes nanofluids highly preferable for designing heat transfer fluids [3].

1.4. Synthesis and Preparation of Nanofluid:

1.4.1. Materials for Nanoparticles and Fluids:

Modern fabrication technology provides great opportunities to process materials actively at nanometer scales. Nanostructured or nanophase materials are made of nanometer-sized substances engineered on the atomic or molecular scale to produce either new or enhanced physical properties not exhibited by conventional bulk solids.

All physical mechanisms have a critical length scale, below which the physical properties of materials are changed. Therefore, particles smaller than100 nm exhibit properties different from those of conventional solids. The noble properties of nanophase materials come from the relatively high surface area/volume ratio, which is due to the high proportion of constituent atoms residing at the grain boundaries [2].

The thermal, mechanical, optical, magnetic, and electrical properties of nanophase materials are superior to those of conventional materials with coarse grain structures. Consequently, research and development investigation of nanophase materials has drawn considerable attention from both material scientists and engineers (Duncan and Rouvray, 1989).

1.4.1.1. Nanoparticle material types: Nanoparticles used in nanofluids have been made of various materials, such as oxide ceramics (Al_2O_3, CuO), nitride ceramics (AlN, SiN), carbide ceramics (SiC, TiC), metals (Cu, Ag, and Au), semiconductors (TiO_2, SiC), carbon nanotubes, and composite materials such as alloyed nanoparticles $Al_{70}Cu_{30}$ or nanoparticle core–polymer shell composites. In addition to nonmetallic, metallic, and other materials for nanoparticles, completely new materials and structures, such as materials "doped" with molecules in their solid–liquid interface structure, may also have desirable characteristics.

1.4.1.2. Host liquid types: Many types of liquids, such as water, ethylene glycol, and oil, have been used as host liquids in nanofluids [2].
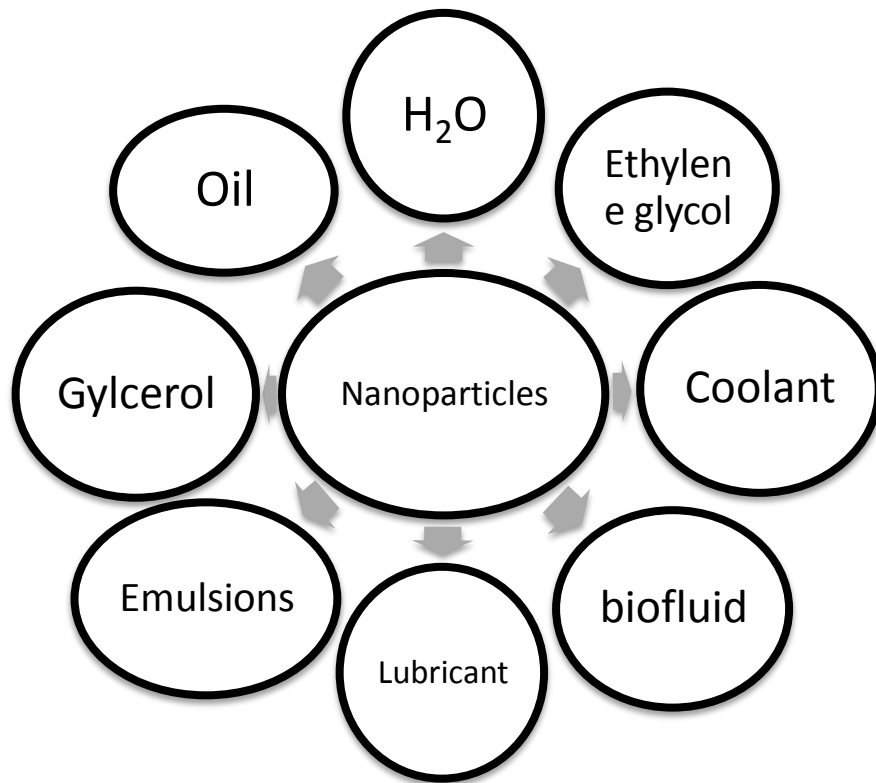
Figure (1.1): A number of liquids (heat transfer fluids) that can host nanoparticles for the production of nanofluids.

1.4.2. Preparation methods:

Preparation methods for nanofluids are mainly two techniques used to produce nanofluids: the single-step and the two-step method.

1.4.2.1. The Single-step Process:

Various methods have been tried to produce different kinds of nanoparticles and nanosuspensions. The initial materials tried for nanofluids were oxide particles, primarily because they were easy to produce and chemically stable in solution. Various investigators have produced Al_2O_3 and CuO nanopowder by an inert gas condensation process that produced 2–200 nm-sized particles. The major problem with this method is its tendency to form agglomerates and its unsuitability to produce pure metallic nanopowders. The problem of agglomeration can be reduced to a good extent by using a direct evaporation condensation method.

Even though this method has limitations of low vapor-pressure fluids and oxidation of pure metals; it provides excellent control over particle size and produces particles for stable nanofluids without surfactant or electrostatic stabilizers [4].

The single-step direct evaporation approach was developed and is called the Vacuum Evaporation onto a Running Oil Substrate technique. The original idea of this method was to produce nanoparticles, but it was difficult to subsequently separate the particles from the fluids to produce dry nanoparticles. A modified vacuum evaporation onto oil technique was developed, in which Cu vapor is directly condensed into nanoparticles by contact with a flowing low-vapor-pressure liquid ethylene glycol [4].

1.4.2.2. The Two Step Process:

The two-step method is extensively used in the synthesis of nanofluids considering the available commercial nano-powders supplied by several companies. In this method, nanoparticles were first produced and then dispersed in the base fluids. Generally, ultrasonic equipment is used to intensively disperse the particles and reduce the agglomeration of particles.

As compared to the single-step method, the two-step technique works well for oxide nanoparticles, while it is less successful with metallic particles. Except for the use of ultrasonic equipment, some other techniques such as control of pH or addition of surface active agents are also used to attain stability of the suspension of the nanofluids against sedimentation. These methods change the surface properties of the suspended particles and thus suppress the tendency to form particle clusters. It should be noted that the selection of surfactants should depend mainly on the properties of the solutions and particles.

For instance, salt and oleic acid as dispersant are known to enhance the stability of transformer oil– Cu and water–Cu nanofluids, respectively. Oleic acid and cetyl trimethyl ammonium bromide (CTAB) surfactants were used to ensure better stability and proper dispersion of TiO_2–water nanofluids.

Sodium dodecyl sulfate (SDS) was used during the preparation of water-based multi wall carbon nanotube dispersed nanofluids since the fibers are entangled in the aqueous suspension. In general, methods such as change of pH value, addition of dispersant and ultrasonic vibration aim at changing the surface properties of suspended particles and suppressing formation of particles cluster to obtain stable suspensions. However, the addition of dispersants can affect the heat transfer performance of the nanofluids, especially at high temperature i.e. in the convective heat transfer and two-phase heat transfer regime [4].

1.4.2.3. Methods for dispersing particles:

Due to the high surface energy of nanoparticles they tend to agglomerate to decrease their surface energy. The agglomeration of nanoparticles causes rapid settling which deteriorates the properties of nanofluids. To keep the nanoparticles from agglomeration they are coated with a surfactant (steric dispersion) or charged to repulse each other in a liquid (electrostatic dispersion). Although the addition of the dispersant could influence the thermal conductivity of the base fluid itself, and thus, the real enhancement by using nanoparticles could be overshadowed.

There are other dispersion methods such as using a high-speed disperser or an ultrasonic probe/bath and also changing the pH value of the suspension (Chopkar et al., 2006). The selection of suitable dispersants depends mainly upon the properties of the solutions and particles and the use of these techniques depends on the required application of the nanofluid. However metallic nanofluids due to their low thermal conductivity have limited interest but metallic nanofluids especially Cu nanofluids and Ag nanofluids due to their high thermal conductivity are the common nanofluids. More specifically we can say that all the metallic nanofluids compared to oxide nanofluids show much more enhancements so that metallic nanofluids and their volume percent is reduced by one order of magnitude at comparable K enhancements. There are a number of factors other than the thermal conductivity of the dispersed phase which should be considered such as the average size of the nanoparticles, the method employed for the preparation of the nanofluids, the temperature of measurements and the concentration of the dispersed solid phase [5].

Table (1.2): The thermal conductivity for some liquids and bulk materials (Mamut 2009)

Material	Thermal Conductivity (W/mK)	Density (Kg/m^3)
Water	0.613	997
Ethylene Glycol	0.252	1114
Engine Oil	0.145	884
Aluminum Oxide	40.0	3970
Silicon	148.0	2330
Aluminum	237.0	2702
Copper	401.0	8933
Gold	317.0	19300
Silver	429.0	10500

The dispersion of copper (Cu) nanoparticles and alternatively carbon nanotubes (CNTs) has provided the most promising results so far, with

reported thermal conductivity enhancements of up to 40% and 160% respectively in relation to the base fluid. Because of the high enhancement of the thermal conductivity of CNT nanofluids [5].

1.5. Mechanisms of Nanofluids:

The conventional understanding of the effective thermal conductivity of mixtures originates from continuum formulations which typically involve only the particle size/shape and volume fraction and assume diffusive heat transfer in both fluid and solid phases. This method can give a good prediction for micrometer or lager-size solid/fluid systems, but it fails to explain the unusual heat transfer characteristics of nanofluids.

The present understanding of thermal transport in nanofluids can be grouped into two categories. Some postulate that the thermal conductivity of nanofluids is composed of the particle's conventional static part and a Brownian motion part which produces micromixing. These models take the particle dynamics into consideration, whose effect is additive to the thermal conductivity of a static dilute suspension. Thus, the particle size, volume fraction, thermal conductivities of both the nanoparticle and the base fluid, and the temperature itself are taken into account in such models for the thermal conductivity of nanofluids.

These theories provide a means of understanding the particle interaction mechanism in nanofluids. Other groups have started from the nanostructure of nanofluids. These investigators assume that the nanofluid is a composite, formed by the nanoparticle as a core, and surrounded by a nanolayer as a shell, which in turn is immersed in the base fluid, and from which a three-component medium theory for a multiphase system is developed. Some have suggested that the enhancement is due to the ordered layering of liquid molecules near the solid particles.

The mechanism for thermal conduction between a liquid and a solid is not clear. To explain the reasons for the anomalous increase of the thermal conductivity in nanofluids, four possible mechanisms were proposed, e.g., Brownian motion of the nanoparticles, molecular-level layering of the liquid at the liquid/particle interface, the nature of heat transport in the nanoparticles, and the effects of nanoparticle clustering, The postulates consider that the effect of Brownian motion can be ignored, since the contribution of thermal diffusion is much greater than Brownian diffusion. However, the postulates only examined the cases of stationary nanofluids.

The thermal conductivities of nanofluids were argued that should be dependent on the microscopic motion and particle structure. Also four possible reasons for the improved effective thermal conductivity of nanofluids were discussed: the increased surface area due to suspended

nanoparticles, the increased thermal conductivity of the fluid, the interaction and collision among particles, the intensified mixing fluctuation and turbulence of the fluid, and the dispersion of nanoparticles [6].

1.6. Characterization of Nanoparticles:

Sizes and physicochemical properties of nanoparticles are closely interrelated and, moreover, are of paramount importance for studying their chemical transformations. Furthermore, there are different approaches to studying the properties of the particles on the surface and in the bulk.

The main techniques used for determining sizes and certain properties of nanoparticles in the gas phase are as follows:
• Ionization by photons and electrons followed by an analysis of the obtained mass spectra by means of quadrupole and time-of-flight mass spectrometers.
• Atomization and selection of neutral clusters with respect to masses.
• Electron transmission microscopy on grids (information on sizes and shapes of particles). To gain information on the particles located on the surface, the following techniques are used:
• Transmission and scanning electron microscopies (TEM, SEM, information on the size/shape of particles, their distribution, and topology);
• Electron diffraction (information on size, phases (e.g., solid/liquid), structure, and bond lengths);
• Adsorption of gases (information on the surface area);
• Photoelectron spectroscopy (determination of the electronic structure);
• Conductivity (information on the conduction band, percolation, and topology).

Miscellaneous techniques are also used for determining sizes and certain properties of nanoparticles in the bulk or within a matrix.

The methods using TEM, SEM, conductivity measurements, and electron diffraction techniques provide information on particles in the bulk, i.e., the data analogous to those obtained for particles on the surface.

Several other techniques are used for studying particles in the bulk. For example, X-ray diffraction can be used for determining particle sizes and internal structures.

Extended X-ray absorption fine structure (EXAFS) technique makes it possible to measure particle sizes; electron paramagnetic (spin) resonance (EPR) and nuclear magnetic resonance (NMR) provide information on the electronic structure. Mössbauer spectroscopy, i.e., the resonance

absorption of gamma quanta by atomic nuclei in solids (gamma resonance), is actively used for gaining insight into the internal structure of a number of elements, especially such important elements as iron. The energy of a gamma quantum is small, and its absorption excites a nucleus. The resonance condition is the equality of the nucleus excitation energy to the energy of a quantum transition, i.e., to the difference between the nucleus internal energy in the excited and ground states.

The transition energy depends on the nature of a nucleus and gives insight into the microscopic structure of solids. The method cannot be applied to all elements; however, it provides valuable information on Fe_{57}, Sn_{119}, and Te_{125} [7].

1.7. The stability of nanofluids:

The agglomeration of nanoparticles results in not only the settlement and clogging of microchannels but also the decreasing of thermal conductivity of nanofluids. So the investigation on stability is also a key issue that influences the properties of nanofluids for application, and it is necessary to study and analyze influencing factors to the dispersion stability of nanofluids [8].

1.7.1. The stability evaluation methods for nanofluids:

1.7.1.1. Sedimentation and centrifugation methods:

Many methods have been developed to evaluate the stability of nanofluids. The simplest method is sedimentation method. The sediment weight or the sediment volume of nanoparticles in a nanofluid under an external force field is an indication of the stability of the characterized nanofluid. The variation of concentration or particle size of supernatant particle with sediment time can be obtained by special apparatus.
The nanofluids are considered to be stable when the concentration or particle size of supernatant particles keeps constant. Sedimentation photograph of nanofluids in test tubes taken by a camera is also a usual method for observing the stability of nanofluids. The tray of sedimentation balance immerged in the fresh graphite suspension. The weight of sediment nanoparticles during a certain period was measured. The suspension fraction of graphite nanoparticles at a certain time could be calculated. For the sedimentation method, long period for observation is the defect. Therefore centrifugation method is developed to evaluate the stability of nanofluids.

The centrifugation method was applied to observe the stability of silver nanofluids which was prepared by the microwave synthesis in ethanol by

reduction of AgNO$_3$ with Poly vinyl pyrrolidone (PVP) as stabilizing agent. It has been found that the obtained nanofluids are stable for more than 1 month in the stationary state and more than 10 h under centrifugation at 3,000 rpm without sedimentation. Excellent stability of the obtained nanofluid is due to the protective role of PVP as it retards the growth and agglomeration of nanoparticles by steric effect. The aqueous polyaniline colloids were prepared, and centrifugation method was used to evaluate the stability of the colloids. Electrostatic repulsive forces between nanofibers enabled the long-term stability of the colloids.

1.7.1.2. Zeta potential analysis:

Zeta potential is electric potential in the interfacial double layer at the location of the slipping plane versus a point in the bulk fluid away from the interface, and it shows the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle. The significance of zeta potential is that its value can be related to the stability of colloidal dispersions. So, colloids with high zeta potential (negative or positive) are electrically stabilized while colloids with low zeta potentials tend to coagulate or flocculate. In general, a value of 25 mV (positive or negative) can be taken as the arbitrary value that separates low-charged surfaces from highly-charged surfaces. The colloids with zeta potential from 40 to 60 mV are believed to be good stable, and those with more than 60 mV have excellent stability. Au nanofluids were prepared with an outstanding stability even after 1 month although no dispersants were observed. The stability is due to a large negative zeta potential of Au nanoparticles in water. The influence of pH and sodium dodecylbenzene sulfonate (SDBS) on the stability of two water-based nanofluids was studied, and zeta potential analysis was an important technique to evaluate the stability. Zhu et al. measured the zeta potential of Al$_2$O$_3$-H$_2$O nanofluids under different pH values and different SDBS concentration. The Derjaguin-Laudau- Verwey-Overbeek (DLVO) theory was used to calculate attractive and repulsive potentials. Cationic gemini surfactant as stabilizer was used to prepare stable water based nanofluids containing Multi-Walled Nanotubes (MWNTs).
Zeta potential measurements were employed to study the absorption mechanisms of the surfactants on the (MWNT) surfaces with the help of Fourier transformation infrared spectra [8].

1.7.1.3. Spectral absorbency analysis:

Spectral absorbency analysis is another efficient way to evaluate the stability of nanofluids. In general, there is a linear relationship between the absorbency intensity and the concentration of nanoparticles in fluid. The dispersion characteristics of alumina and copper suspensions were

evaluated using the conventional sedimentation method with the help of absorbency analysis by using a spectrophotometer after the suspensions deposited for 24 h.

The stability investigation of colloidal Fe/Pt nanoparticle systems was done via spectrophotometer analysis. The sedimentation kinetics could also be determined by examining the absorbency of particle in solution .If the nanomaterials dispersed in fluids have characteristic absorption bands in the wavelength 190-1100 nm, it is an easy and reliable method to evaluate the stability of nanofluids using UV-Vis spectral analysis. The variation of supernatant particle concentration of nanofluids with sediment time can be obtained by the measurement of absorption of nanofluids because there is a linear relation between the supernatant nanoparticle concentration and the absorbance of suspended particles.
The outstanding advantage comparing to other methods is that UV-Vis spectral analysis can present the quantitative concentration of nanofluids.

The stability of nanofluids was studied with the UV- Vis spectrophotometer. It was believed that the stability of nanofluids was strongly affected by the characteristics of the suspended particles and the base fluid such as particle morphology. Moreover, addition of a surfactant could improve the stability of the suspensions. The relative stability of Multi-Walled Nanotubes (MWNT) nanofluids could be estimated by measuring the UV- Vis absorption of the MWNT nanofluids at different sediment times. From the above relation between MWNT concentration and its UV- Vis absorbance value the concentration of the MWNT nanofluids at different sediment times could be obtained.

The above three methods can be united to investigate the stability of nanofluids. For example, the dispersion behavior of the aqueous copper nano-suspensions under different pH values, different dispersant type and concentration was evaluated by the method of zeta potential, absorbency and sedimentation photographs.

1.7.2. The ways to enhance the stability of nanofluids:

1.7.2.1. Surfactants used in nanofluids:

Surfactants used in nanofluids are also called dispersants. Adding dispersants in the two phase systems is an easy and economic method to enhance the stability of nanofluids. Dispersants can markedly affect the surface characteristics of a system in small quantity. Dispersants consists of a hydrophobic tail portion, usually a long-chain hydrocarbon, and a hydrophilic polar head group. Dispersants are employed to increase the contact of two materials, sometimes known as wet ability. In a two-phase system, a dispersant tends to locate at the interface of the two phases, where it introduces a degree of continuity between the nanoparticles and

fluids. According to the composition of the head, surfactants are divided into four classes: non-ionic surfactants without charge groups in its head (include polyethylene oxide, alcohols, and other polar groups); anionic surfactants with negatively charged head groups (anionic head groups include long-chain fatty acids, sulfosuccinates, alkyl sulfates, phosphates, and sulfonates); cationic surfactants with positively charged head groups (cationic surfactants may be protonated long-chain amines and long-chain quaternary ammonium compounds); and amphoteric surfactants with zwitterionic head groups (charge depends on pH. The class of amphoteric surfactants is represented by betaines and certain lecithins). How to select suitable dispersants is a key issue. In general, when the base fluid of nanofluids is polar solvent, we should select water soluble surfactants, otherwise we will select oil soluble.

For nonionic surfactants, we can evaluate the solubility through the term hydrophilic/lipophilic balance (HLB) value. The lower the HLB number the more oil soluble the surfactants, and in turn the higher the HLB number the more water-soluble the surfactants is. The HLB value can be obtained easily by many handbooks [8].

1.7.2.2. Surface modification techniques-surfactant free method:

Although surfactant addition is an effective way to enhance the dispersibility of nanoparticles, surfactants might cause several problems. For example, the addition of surfactants may contaminate the heat transfer media. Surfactants may produce foams when heating, while heating and cooling are routinely processes in heat exchange systems. Furthermore surfactant molecules attaching on the surfaces of nanoparticles may enlarge the thermal resistance between the nanoparticles and the base fluid, which may limit the enhancement of the effective thermal conductivity. Use of functionalized nanoparticles is a promising approach to achieve long-term stability of nanofluid. It represents the surfactant free technique. A work on the synthesis of functionalized silica (SiO_2) nanoparticles was presented by grafting silanes directly to the surface of silica nanoparticles in original nanoparticle solutions. One of the unique characteristics of the nanofluids was that no deposition layer formed on the heated surface after a pool boiling process. Hydrophilic functional groups on the surface of the nanotubes were introduced by mechanochemical reaction. The prepared nanofluids, with no contamination to medium, good fluidity, low viscosity, high stability, and high thermal conductivity, would have potential applications as coolants in advanced thermal systems. A wetmechanochemical reaction was applied to prepare surfactant-free nanofluids containing double- and single-walled carbon nanotubes. Results from the infrared spectrum and zeta potential measurements showed that the hydroxyl groups had been introduced onto the treated

carbon nanotubes surfaces. Plasma treatment was used to modify the surface characteristics of diamond nanoparticles. Through plasma treatment using gas mixtures of methane and oxygen, various polar groups were imparted on the surface of the diamond nanoparticles, improving their dispersion property in water. A stable dispersion of titania nanoparticles in an organic solvent of diethylene glycol dimethylether was successfully prepared using a ball milling process. In order to enhance dispersion stability of the solution, surface modification of dispersed titania particles was carried out during the centrifugal bead mill process. Surface modification was utilized with silane coupling agents, trimethoxysilane and trimethoxypropylsilane. Zinc oxide nanoparticles could be modified by polymethacrylic acid (PMAA) in aqueous system. The hydroxyl groups of nano-ZnO particle surface could interact with carboxyl groups of PMAA and form poly (zinc methacrylate) complex on the surface of nano-ZnO. PMAA enhanced the dispersibility of nano-ZnO particles in water. The modification did not alter the crystalline structure of the ZnO nanoparticles [8].

1.7.2.3. Stability mechanisms of nanofluids:

Particles in dispersion may adhere together and form aggregates of increasing size which may settle out due to gravity. Stability means that the particles do not aggregate at a significant rate. The rate of aggregation is in general determined by the frequency of collisions and the probability of cohesion during collision. Derjaguin, Verway, Landau and Overbeek (DVLO) developed a theory which dealt with colloidal stability. DLVO theory suggests that the stability of a particle in solution is determined by the sum of Van der Waals attractive and electrical double layer repulsive forces that exist between particles as they approach each other due to the Brownian motion they are undergoing. If the attractive force is larger than the repulsive force, the two particles will collide, and the suspension is not stable. If the particles have a sufficient high repulsion, the suspensions will exist in stable state. For stable nanofluids or colloids, the repulsive forces between particles must be dominant. According to the types of repulsion, the fundamental mechanisms that affect colloidal stability are divided into two kinds, one is steric repulsion, and another is electrostatic repulsion. For steric stabilization, polymers are always involved into the suspension system, and they will adsorb onto the particles surface, producing an additional steric repulsive force. For example, Zinc oxide nanoparticles modified by polymethacrylic acid (PMAA) have good compatibility with polar solvents. Silver nanofluids are very stable due to the protective role of Poly vinyl pyrrolidone (PVP) as it retards the growth and agglomeration of nanoparticles by steric effect. PVP is an efficient agent to improve the stability of graphite suspension. The steric effect of polymer dispersant is determined by the

concentration of the dispersant. If the PVP concentration is low, the surface of the graphite particles is gradually coated by PVP molecules with the increase of PVP. The effect of polymer dispersant structure on electrosteric interaction and dense alumina suspension behavior was studied. An optimum hydrophilic to hydrophobic group ratio was obtained from the maximum repulsive force and minimum viscosity [8].

1.7.3. Aggregation control in nanofluids:

The preceding studies have shown that, to control the agglomeration of nanoparticles (NPs) in the suspension and avoid settling, it is recommended to use:

• Viscous host fluids with high value of the dielectric constant, low particles volume fraction φ and not too small particles.
• Pure highly des-ionized water with low values of the ionic strength.
• PH outside the region of the isoelectric point for the case of amphoteric NPs suspended in water. The isoelectric point (IEP) may be defined as the pH at which the surface of the NP exhibits a neutral net electrical charge or equivalently a zero zeta potential $\zeta = 0$ V. For this particular value of ζ there are only attractive forces of Van der Waals and the solution is not stable. For example in the case of copper oxide NPs suspended in water, IEP (CuO) $\approx$ 9.5 at RT and a neutral or acid pH _ 7 promotes the stability of the suspension.
• Surface coating with surfactants or with low molecular weight (Mw < 10000) neutral polymers highly soluble in the liquid suspension. They allow saturating the surface of NPs without affecting the long range repulsive electrostatic force. In contrast this polymeric shell induces steric effects that may dominate the short distances attractive Van der Waals interaction. Thus forces are always repulsive and the solution is stable. In a sense the presence of the polymer shell enhances the value of the energy barrier Eb.
• High power sonication to break agglomerates and disperse particles. It is important to mention here that the surface treatments we presented above allow to enhance the stability of the suspension and to control the aggregation, but unfortunately they certainly also have a deep impact on the heat transfer properties of the nanofluid and should be considered carefully. The control of the NPs surface using polymer coating, surfactants or ions grafting, introduces unknown thermal interfacial resistances which can dramatically alter the benefit of using highly conductive nanoparticles [9].

1.8. Thermophysical Properties of Nanofluids:

There are four thermophysical properties related to fluid, which are namely density, viscosity, specific heat capacity and thermal conductivity.

1.8.1. Density:

The density, or more precisely, the volumetric mass density, of a substance is its mass per unit volume. The symbol most often used for density is ρ (the lower case Greek letter rho), although the Latin letter D can also be used. Mathematically, density is defined as mass divided by volume [10].

$$\rho = \frac{m}{V} \qquad (9)$$

Where **ρ** is the density, **m** is the mass, and **V** is the volume. In some cases (for instance, in the United States oil and gas industry), density is loosely defined as its weight per unit volume [11] , although this is scientifically inaccurate – this quantity is more specifically called specific weight.
For a pure substance the density has the same numerical value as its mass concentration. Different materials usually have different densities, and density may be relevant to buoyancy, purity and packaging. Osmium and iridium are the densest known elements at standard conditions for temperature and pressure but certain chemical compounds may be denser.

To simplify comparisons of density across different systems of units, it is sometimes replaced by the dimensionless quantity "relative density" or "specific gravity", i.e. the ratio of the density of the material to that of a standard material, usually water, Thus a relative density less than one means that the substance floats in water.

The density of a material varies with temperature and pressure. This variation is typically small for solids and liquids but much greater for gases. Increasing the pressure on an object decreases the volume of the object and thus increases its density. Increasing the temperature of a substance (with a few exceptions) decreases its density by increasing its volume. In most materials, heating the bottom of a fluid result's in convection of the heat from the bottom to the top, due to the decrease in the density of the heated fluid. This causes it to rise relative to more dense unheated material.

The reciprocal of the density of a substance is occasionally called its specific volume, a term sometimes used in thermodynamics. Density is an

intensive property in that increasing the amount of a substance does not increase its density; rather it increases its mass [11].

Density measurements were performed by Vajjha et al. (2009) on three different nanofluids containing Al_2O_3 (44 nm), antimony tin oxide, $Sb_2O_5:SnO_2$ (22–44 nm), and ZnO (70 nm) nanoparticles in a base fluid of 60:40 Ethylene Glycol/water by mass over a temperature range of 0–50 °C for concentration range of 1–10 %. A good agreement is observed between the measured values with Eq. (10) of Pak and Cho 1998 (1998) at all temperatures and concentrations for Al_2O_3 and $Sb_2O_5:SnO_2$ with maximum deviation of 1.2 %. However, a maximum deviation of 8.0 % is observed with ZnO nanofluid [12].

$$\rho_{nf} = \emptyset_p \ \rho_p + (1+\emptyset) \ \rho_{bf} \qquad (10)$$

Where ρ_{nf} denstiy of nanofluid, $\emptyset$ Volume fraction of nanoparticles, ρ_p density of nanoparticles, ρ_{bf} density of base fluid

The following observations can be made from the investigations undertaken on nanofluid density:

• The nanofluid density is higher than that of the base liquid.
• The nanofluid density increases with concentration.
• The density of nanofluid decreases with the increase in temperature [12].

1.8.2. Viscosity:

Viscosity is a property of the fluid which opposes the relative motion between the two surfaces of the fluid that are moving at different velocities. In simple terms, viscosity means friction between the molecules of fluid. When the fluid is forced through a tube, the particles which compose the fluid generally move more quickly near the tube's axis and more slowly near its walls; therefore some stress is needed to overcome the friction between particle layers to keep the fluid moving. For a given velocity pattern, the stress required is proportional to the fluid's viscosity.

A fluid that has no resistance to shear stress is known as an ideal or in viscid fluid. Zero viscosity is observed only at very low temperatures in superfluids. Otherwise, all fluids have positive viscosity and are technically said to be viscous or viscid. A fluid with a relatively high viscosity, such as pitch, may appear to be a solid [13].

1.8.2.1. Viscosity Models:

The earliest studies for the determination of viscosity of suspended particles in liquids were undertaken by Einstein. An equation has been

proposed based on the liquid particle interaction, which can predict the effective viscosity of liquid for volume concentrations lower than 1.0 %.

The Einstein's equation is given by Eq. (1):

$$\mu_r = \frac{\mu_{nf}}{\mu_w} = (0.1+2.5\emptyset) \qquad (1)$$

$$\mu_r = \frac{\mu_{nf}}{\mu_w} = \left(\frac{1-\emptyset}{\emptyset m}\right)^{-[\eta]\emptyset m} \qquad (2)$$

Where η is the intrinsic viscosity, 2.5 for solid spheres and $\emptyset m$ is the maximum packing fraction. The maximum close-packing fraction is approximately 0.64 for randomly monodispersed spheres.

$$\emptyset = \left(\frac{a_a}{a}\right)^{3-D} \qquad (3)$$

$$\mu_r = \frac{\mu_{nf}}{\mu_w} = \left(1 - \frac{\emptyset}{\emptyset_m}\left(\frac{a_a}{a}\right)^{1.2}\right)^{-[\eta]\emptyset_m} \qquad (4)$$

Where a_a and a are the radii of aggregates and primary nanoparticles, respectively. The term D is defined as the fractal index, which for nanoparticles a typical value of 1.8 has given by Chen et al. (2007).

Junming et al. (2002) have measured the viscosity of CuO nanoparticles dispersed in water with the particle concentration range of 2–10 % and in the temperature range of 30–80 °C. The viscosity of the suspensions was reported to be higher than that of water by 15–30 %.

Based on the studies undertaken by various investigators, the following observations can be deduced for nanofluids in base liquid water, Ethylene Glycol (EG), and EG/water mixtures.

• Newtonian behavior is observed for volume concentration lower than 4 % in the temperature range of 20–70 °C.
• Viscosity increases with the increase in concentration of the nanofluid.
• Viscosity of the nanofluid decreases with the increase in temperature.
• Viscosity increases with the decrease in particle size which is observed by most of the investigators.
• Viscosity enhancement in base liquid EG is reported by many investigators to be higher than that with water.
• The nature of material may not have significant influence on nanofluid viscosity [12].

1.8.3. Specific Heat:

Heat capacity or thermal capacity is a measurable physical quantity equal to the ratio of the heat added to (or removed from) an object to the resulting temperature change [14]. The unit of heat capacity is joule per kelvin J/K, or kilogram metre squared per kelvin second squared $(Kg.m^2/Ks^2)$ in the International System of Units (SI).

Specific heat is the amount of heat needed to raise the temperature of one kilogram of mass by 1 kelvin.

Heat capacity is an extensive property of matter, meaning that it is proportional to the size of the system. When expressing the same phenomenon as an intensive property, the heat capacity is divided by the amount of substance, mass, or volume, thus the quantity is independent of the size or extent of the sample.

The molar heat capacity is the heat capacity per unit amount (SI unit: mole) of a pure substance, and the specific heat capacity, often called simply specific heat, is the heat capacity per unit mass of a material. Nonetheless some authors use the term specific heat to refer to the ratio of the specific heat capacity of a substance at any given temperature to the specific heat capacity of another substance at a reference temperature, much in the fashion of specific gravity. In some engineering contexts, the volumetric heat capacity is used.

Temperature reflects the average randomized kinetic energy of constituent particles of matter relative to the centre of mass of the system, while heat is the transfer of energy across a system boundary into the body other than by work or matter transfer. Translation, rotation, and vibration of atoms represent the degrees of freedom of motion which classically contribute to the heat capacity of gases, while only vibrations are needed to describe the heat capacities of most solids [15].

According to Wang et al. (2006), specific heat capacity of a particle varies with particle size. Since smaller particles have larger specific surface areas, the influence of surface energy on the effective specific heat capacity increases with a reduction in particle size. Ping Zhou et al. (2010) showed the deviation of specific heat capacity of CuO/ Ethylene Glycol (EG) nanofluid at different volume concentrations evaluated using equations given by Eqs. (7) And (8) with their experimental data.

$$Cp_{nf} = \frac{(1-\emptyset)(\rho Cp)_{pf} + \emptyset\ (\rho Cp)_p}{(1-\emptyset)\rho_{pf} + \rho p} \qquad (7)$$

$$Cp_{nf} = \emptyset\ Cp + (1-\emptyset)\ C_{bf} \qquad (8)$$

The following observations can be made from the investigations undertaken on nanofluid specific heat:

• The nanofluid specific heat is lower than the values of base liquid.
• The specific heat of nanofluid decreases with the increase in concentration.
• The specific heat of nanofluid does not vary significantly with temperature.
• The deviation in the values of heat capacity of nanofluids for different sizes of nanoparticles is insignificant with increasing volume concentration, due to the large heat capacity of the base fluid. Hence, the variation of heat capacity with volume concentration is a constant [12].

1.8.4. Thermal Conductivity:

Thermal conductivity (often denoted k, λ, or κ) is the property of a material to conduct heat. It is evaluated primarily in terms of the Fourier's Law for heat conduction. In general, thermal conductivity is a tensor property, expressing the anisotropy of the property.

Heat transfer occurs at a lower rate in materials of low thermal conductivity than in materials of high thermal conductivity. Correspondingly, materials of high thermal conductivity are widely used in heat sink applications and materials of low thermal conductivity are used as thermal insulation. The thermal conductivity of a material may depend on temperature. The reciprocal of thermal conductivity is called thermal resistivity.

The reciprocal of thermal conductivity is thermal resistivity, usually expressed in kelvin-meters per watt ($K \cdot m \cdot W^{-1}$). For a given thickness of a material, that particular construction's thermal resistance and the reciprocal property, thermal conductance, can be calculated. Unfortunately, there are differing definitions for these terms [16].

Thermal conductivity, k, often depends on temperature. Therefore, the definitions listed below make sense when the thermal conductivity is temperature independent. Otherwise a representative mean value has to be considered; for more, see the equations section below [16].
The equation of Hamilton and Crosser (1962) is widely used for comparison of the experimental data by various investigators. The equation for determining the nanofluid thermal conductivity is given by:

$$k_{nf} = k_{bf} \left[\frac{k_b + (n-1)k_b - \emptyset(n-1)(k_{bf} - k_b)}{k_b + (n-1)k_{bf} + \emptyset(k_{bf} - k_b)} \right] \quad (5)$$

Where the empirical shape factor 'n' is equal to $3/\psi$ and ψ the sphericity.

Sphericity is defined as the ratio of the surface area of a sphere with the volume equal to that of the average particle, to the surface area of the particle.

The experimental observations indicate the dependence of material, concentration, particle size, temperature, and the influence of pH value on nanofluid thermal conductivity.

It can be observed that most of the investigators who improved Maxwell's models used certain empiricism in their equations. Early determination of nanofluid thermal conductivity through experiments was undertaken using base liquid as water.

Pak and Cho (1998) determined the thermal conductivity of Al_2O_3 and TiO_2 nanofluids at 27 °C which can be presented as:

$$k_{nf} = (1+7.47\emptyset)k_{bf} \quad (6) \ [12]$$

The following observations can be made from the investigations undertaken:

• The thermal conductivity of metal and oxide nanofluids is observed to be greater than that of equivalent macroparticle suspensions.

• Experiments for the determination of nanofluid thermal conductivity are undertaken mostly with spherical particles having diameters in the range of 20– 300 nm and temperature between 20 and 70 °C having Newtonian properties for a maximum volume concentration of 4.0 % in base liquid water, Ethylene Glycol (EG), and EG/water mixtures.

• Experimental data have confirmed higher thermal conductivities than the base liquid which increases with concentration and temperature.

• The conductivity ratios of ethylene glycol-based nanofluids are reported to be higher than those of water-based nanofluids.

• Metal nanofluids have higher enhancements than those of oxide nanofluids.

• Nanofluid thermal conductivity is relatively higher at lower volume fractions, thereby giving a nonlinear dependence on particle volume fraction.

• The experimental results indicate the thermal conductivity ratio to increase linearly with volume fraction, but with different rates of increase for each nanofluid.

• Nanofluid thermal conductivity is observed to depend on particle size and suspension temperature.

• Material properties influence the thermal conductivity of nanofluids leading to higher enhancements compared to viscosity. This observation may vary with temperature, nanofluid concentration, and particle size [12].

1.9. Application of nanofluids

1.9.1. Heat transfer Intensification

Since the origination of the nanofluid concept about a decade ago, the potentials of nanofluids in heat transfer applications have attracted more and more attention. Up to now, there are some review papers, which present overviews of various aspects of nanofluids, including preparation and characterization, techniques for the measurements of thermal conductivity, theory and model, thermophysical properties, convective heat transfer. In this part, we will summarize the applications of nanofluids in heat transfer enhancement [8].

   i.   Industrial cooling applications:

The application of nanofluids in industrial cooling will result in great energy savings and emissions reductions. For US industry, the replacement of cooling and heating water with nanofluids has the potential to conserve 1 trillion Btu of energy. For the US electric power industry, using nanofluids in closed loop cooling cycles could save about 10-30 trillion Btu per year (equivalent to the annual energy consumption of about 50,000–150,000 households). The associated emissions reductions would be approximately 5.6 million metric tons of carbon dioxide, 8,600 metric tons of nitrogen oxides, and 21,000 metric tons of sulfur dioxide.

Experiments were performed using a flow-loop apparatus to explore the performance of polyalphaolefin nanofluids containing exfoliated graphite nanoparticle fibers in cooling. It was observed that the specific heat of nanofluids was found to be 50% higher for nanofluids compared with polyalphaolefin and it increased with temperature. The thermal diffusivity was found to be 4 times higher for nanofluids.

The convective heat transfer was enhanced by ~10% using nanofluids compared with using polyalphaolefin. Ma et al. proposed the concept of nano liquid-metal fluid, aiming to establish an engineering route to make the highest conductive coolant with about several dozen times larger thermal conductivity than that of water. The liquid metal with low melting point is expected to be an idealistic base fluid for making super conductive solution which may lead to the ultimate coolant in a wide variety of heat transfer enhancement area. The thermal conductivity of the liquid-metal fluid can be enhanced through the addition of more conductive nanoparticles [8].

   ii.   Electronic applications
   iii.   Transportation
   iv.   Space and defense
   v.   Heating buildings and reducing pollution
   vi.   Nuclear systems cooling

1.9.2. Mass transfer enhancement

Several researches have studied the mass transfer enhancement of nanofluids. Kim et al. initially examined the effect of nanoparticles on the bubble type absorption for NH_3/H_2O absorption system. The addition of nanoparticles enhances the absorption performance up to 3.21 times.

Then they visualized the bubble behavior during the NH_3/H_2O absorption process and studied the effect of nanoparticles and surfactants on the absorption characteristics. The results show that the addition of surfactants and nanoparticles improved the absorption performance up to 5.32 times.

The addition of both surfactants and nanoparticles enhanced significantly the absorption performance during the ammonia bubble absorption process. The theoretical investigations of thermodiffusion and diffusionthermo on convective instabilities in binary nanofluids for absorption application were conducted. Mass diffusion is induced by thermal gradient. Diffusionthermo implies that heat transfer is induced by concentration gradient.

The mass transfer process of absorption was studied using CNTs-ammonia nanofluids as the working medium. The absorption rates of the CNTs-ammonia binary nanofluids were higher than those of ammonia solution without CNTs. The effective absorption ratio of the CNTs-ammonia binary nanofluids increased with the initial concentration of ammonia and the mass fraction of CNTs [8].

1.9.3. Energy applications
  i.   Solar absorption
 ii.   Energy storage

1.9.4. Mechanical applications
  i.   Magnetic sealing
 ii.   Friction reduction

1.9.5. Biomedical application
  i.   Nanodrug delivery
 ii.   Antibacterial activity [8].

1.10. Copper oxide nanoparticles:

Copper oxide (CuO) is one of potential p-type semiconductors and gains considerable attentions due to its excellent optical, electrical, physical, and magnetic properties.

CuO with narrow band gap of 1.2 eV is extensively used in various applications such as catalysis, solar energy conversion, gas sensor and field emission. However, these novel properties can be improved by synthesis in CuO nanostructures that shown excellent performance comparing to bulk counterpart.

Different nanostructures of CuO are synthesized in form of nanowire, nanorod, nanoneedle, nano-flower and nanoparticle. In the past decades, various methods have been proposed to produce CuO nanoparticles with different sizes and shapes such as thermal oxidation, sonochemical, combustion and quick-precipitation.

Among these processes, precipitation method is a facile way which attracts considerable interest in industries because of low energy and temperature, inexpensive and cost-effective approach for large scale production and good yield [17].

1.11. Literature Review:

An extensive evaluation of the electrical conductivity of nanoparticles made up of metallic and ceramic nanoparticles (Cu, Al_2O_3, and CuO) with volume fractions in different regimes were performed. Thus, it was observed that the electrical conductivity increases with both particle concentration and particle size reduction, in case of water and ethylene-glycol based nanofluids. It is also argued that the electrical conductivity enhancement is higher in case of ceramic nanofluids than metallic ones because of the effective dielectric constant and density. It is also emphasized that the use of surfactant increases the stability, which in turn decreases the conductivity due to its higher viscosity in turn. Also, it is observed that the conductivity increases at lower concentrations of electrolyte than at higher concentrations where it shows an in turn lower value. These observations are then compared with the ones proposed in the model of O'Brien for electrical conductivity of suspensions. Also, it was eventually observed that there was no significant influence of fluid temperature on the conductivity [18].

A one-parameter model concerning the electrical conductivity of dispersed metallic nanofluids was presented. It takes the decreasing size of metallic nanoparticles and the consequent decrease in electrical conductivity into account. But, although all of this was done, still the effect of size of nanoparticles on thermal conductivity could not be elucidated precisely. Thus, the thermal conductivity of six silver nanofluids was reported with varying volume fractions. As a result of this, it was deduced that the decreasing thermal conductivity had to be taken into brief account for the development of further thermal conductivity models [19].

A brief study on the varied applications of nanofluids, as in, coolant in the diesel electric generator (DEG) was presented. The specific heat of aluminium oxide with varied particle sizes had been measured, indicating their decrease with increase in temperature and concentration. Widespread experiments were performed to assess the co-generation efficiency of the DEG. Thus, there showed a decrease in its value on applying nanofluids. This resulted due to a decrease in the specific heat, which influenced the waste heat recovery from the system, which in turn increased in the effect of the nanofluids, as a result of its superior convective heat and radiative heat properties [20].

An experiment for the effective electrical conductivity measurement of aluminium oxide nanoparticles suspensions was performed. These were performed as a function of volume fraction as well as temperature to examine their respective effects. Thus, the results that were reported

indicated considerable enhancement of the value with increase in both of the fractions. But, it was observed that the effect of temperature was much more pronounced than that of volume fraction [21].

The efficacy of nanofluids as coolants was investigated and indicated that the thermo-physical properties were considerably affected by nanoparticle addition to the base-fluid. In this regard, a 4% CuO suspension in water is selected. Then its performance on a plate heat exchanger (PHE) was studied. The studies gave rise to the fact that the flow in the exchanger also affects the coolant efficacy. Thus, the fluid viscosity comes out to be a crucial factor. Thus, it was concluded that for large volume fractions, nanofluids are not the suitable replacement [22].

The recent advancements in nanofluids was reviewed, with special emphasis on the associated material properties and its corresponding effect on thermal conductivity and other thermal properties and the novel approaches to achieving a high value of the associated properties. This task was taken up by him in order to resolve the high degree of ambiguity surrounding the high promise as was expected in case of nanofluids. The high scale miniaturization of the particles which led to the high-scale properties have been quite precisely described in the study. The associated problems of low conductivity, both thermal and electrical, led to this study being of high-scale prominence [23].

A novel one-stop method for the preparation of copper nanofluids was presented from its associated sulphide, $CuSO_4.5H_2O$ using $NaH_2PO_2.H_2O$ in ethylene glycol under very irradiation in the microwave scale. Highly non-agglomerated and highly stable nanofluids were obtained. The effects of the different reacting agents, i.e., the complexes and the microwave irradiation were observed precisely under a transmission electron microscope (TEM) and associated infrared and sedimentary analysis. It was ultimately found to be one of the most effective and rapid one-step solutions for preparing Cu nanofluids [24].

Ahead in regards of determining the varied limiting factors was worked in order to push ahead the development of nanofluids. It was taken up in order to fasten the stagnating scope of research in the field, since the time it had been formulated regarding enhanced electrical conductivity [25].
The fabrication, the associated thermal conductivity and the varied rheological properties of nanofluids comprising of copper nanoparticles in diethylene glycol base were investigated. The fabricated fluids exhibited enhanced thermal conductivity. This was formed by directly forming the nanoparticles in the ethylene base fluid, by means of assisted microwave heating, which accelerated the clusters of metal to monodispersed nanostructures. The particles exhibited an average size of 75 ± 25 nm for SEM micrographs, which aggregated to form spherical

agglomerates within the size range of 300 nm. The various physicochemical properties, thermal conductivity and viscosity included, were measured in the size range of 0.4-1.6 % weight fraction of nanoparticles within the range of 20-5- Celsius. The correlational models, appropriate to the system, were applied to compare the associated properties, which were rather found to be higher in case of thermal conductivity enhancement than the viscosity counterpart. Thus, it showed that with changing concentrations, the thermal properties display more pronounced variation than in the case of viscosity [26].

The detailed analysis regarding the synthesis of very low concentration comprising nanofluids were reported, the most common ways being one-step and two-step methods. While, stable nanofluids can be produced with wide concentrations in case of the one-step method, the two-step provides a means to produce nanofluids with widespread dispersity. In spite of all this, the central point lies the thermal conductivity of the fluids, which is the most researched aspect all around the globe. In this study, an insight has been presented into the different factors which affect this really crucial property of the nanofluids. Along with it, has been presented how the theories that existed explain the anomaly regarding the enhancement of the thermal conductivity of the fluids. Thus, it provides a widely varying view of the different aspects that lead to the sole concept of nanofluids, may it be with regards to physical or the associated theoretical and experimental regards which support the whole background of experiments and developments that led to its wholesome evolution [27].

The thermal storage characteristics of $Cu-H_2O$ nanofluids as phase changing material (PCM) in case of cooling systems were investigated. Varied experiments were carried out to study the influence of the sole nanoparticle agent in the supercoiling of PCM which are highly water based. The associated temperature shape and ice shape were observed over the web using infrared heat camera and color digital camera. A mechanism to improve the thermal characteristics was devised by measuring the contact angle and their thermal conductivity. Thus, the experimental results showed that the $Cu-H_2O$ system showed a considerably lower degree of supercoiling than the water PCMs. On addition of 0.1 wt. % of nanoparticles, the degree of supercoiling was reduced by about 20.5%, whereas the freezing time got reduced by about 19.2 %. Thus, these results showed the highly promising and widely diverse applications of nanofluids, when their thermal distributions are taken into account [28].

The thermal performance of a flat CPL was investigated using water based and ethanol based Cu nanofluids under several steady sub-atmospheric working systems. This was done with the evaporator of the

CPL horizontally placed and bottom-heated. Thus, the results showed that on addition of Cu the evaporating heat coefficient gets highly enhanced along with the maximum heat removing capacity of the system. But, there is an optimal concentration of the particles at which we observe the highest coefficient and it decreases with further increase in the concentration. Along with, the coefficient increases drastically with the operating temperature of the system. The coefficient and the heat removal capacity consequently can be increased upto levels of 45% and 16% respectively when substituted with ethanol-bas fluids [29].

The recent researches were summarized with the trends of synthesis, their associated thermo-physical properties, their related heat transfer properties and their consequential pressure-drop characteristics. They showed that with proper hybridization, the properties of the hybrid nanofluids could be so tailored as to become promising enough for heat transfer enhancement and associated thermal properties along with it. This study was taken up in order to overcome the problems and limitations faced by the conventional nanofluids and to find a mid-way in order to enhance their properties without losing their base characters. In spite of all the ups and downs in its research type, it has highly emerged as a very promising fluid which is very effective when it comes to heat transfer and the same goes for acting as a coolant in different systems under highly varying condition [30].

1.12. The Aim of Study:

The objectives of the present study are:

- To prepare Copper Oxide nanoparticles and characterize the obtained metal oxide nanoparticles using IR- spectrometer and UV/Vis spectrometer.

- To disperse the prepared Copper Oxide nanoparticles in de-ionized water using ultrasonic probe/bath to form nanofluid.

- To study thermophysical properties: density, viscosity, specific heat capacity and thermal conductivity.

- To study the stability for the prepared Copper Oxide-Water nanofluid by sedimentation method.

Chapter Two

Materials and Methods

Chapter two
Materials and Methods

2.1. Materials

2.1.1. Chemicals:

Copper nitrate tri-hydrate (Cu $(NO_3)_2.3H_2O$), De-ionized water, Ammonium Hydroxide (NH_4OH, 25%), Ethanol (C_2H_5OH, 99.8%), Potassium bromide (KBr, Powder).

All the chemicals used in were of analytical grade type.

2.1.2. Instruments and Equipments:

- Magnetic stirrer /hot plate
- Sensitive Balance: SHIMADZU, Electronic Balance, Type: AY120, NO. D432711233, Made in Japan
- Ultrasonic vibration instrument: Transonic T 460, 35Hz
- Infra-Red Spectroscopy (IR): JASCO, FT/IR-4100LE Serial No. B18736106, protect: Class1, Made in Japan
- UV spectrometer (Lamda 20; PerkinElmer)
- Pychnometer
- Rheometer (Contraves LS 40)
- Differential scanning calorimeter (TA Instruments Q2000)
- Autobalance (Perkin Elmer AD6)
- Thermometer
- Hot plate (350 W)
- Condenser system

2.1.3. Glass wares:

- All glass ware were Pyrex type

2.2. Methods:

2.2.1. Preparation of Copper Oxide Nanoparticles:

25g of copper nitrate tri-hydrate was dissolved in 200 ml de-ionized water in a beaker (500ml). The Blue solution of Cu $(NO_3)_2.3H_2O$ was stirred and heated $(150 – 200)\,°C$ with magnetic stirrer /hot plate. After 10 minutes, about 65ml of ammonium hydroxide were added drop by drop to the solution. During the addition of the base the solution's color was changed from blue to dark brown also black precipitate was occurred. The addition was stopped after the solution's color turn black and it was stirred and heated for an hour and half. When the solution was cool down the black precipitate was filtered by filter paper and washed twice with water and twice with ethanol. The precipitate was dried by air for 24h.

$$Cu(NO_3)_2 + 2NH_4OH \rightarrow Cu(OH)_2 + 2NH_4NO_3$$

$$Cu(OH)_2 \xrightarrow{\Delta} CuO + H_2O$$
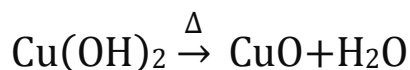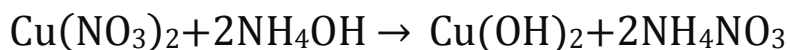
1) $Cu(NO_3)_2$ Solution (before addition) 2) During the addition of NH_4OH 3) After the end of the addition 4) CuO nanopowder

2.2.2. Preparation of Copper Oxide Nanofluids:

Specific amount of Copper Oxide nanoparticles were dispersed in 50 ml de-ionized water to prepare CuO/water nanofluid. The prepared CuO/water nanofluid was subjected by ultrasonic vibration instrument for about 2 hours.

Table (2.1): concentrations and weights of nanofluid samples:

Wt %	Weight (g) in 50ml	Volume fraction	Volume fraction %
1	0.5014	0.0016	0.16
2	1.0010	0.0032	0.32
3	1.5004	0.0047	0.47
5	2.5017	0.0079	0.79
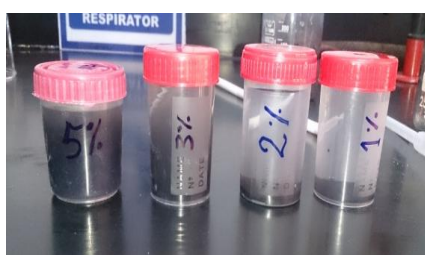
1) before ultrasonic

2) during mixing in ultrasonic instrument

3) after mixing

2.2.3. Characterization of Copper Oxide Nanoparticles:

2.2.3.1. Fourier Transform Infrared Spectroscopy:

2mg of the Copper Oxide nanoparticles were triturated with 300 mg of dried potassium bromide. These quantities were usually sufficient to given a suitable intensity of spectrum when use a disc with diameter (10-15mm). Carefully the mixture was grinded, spread uniformly in a suitable disc, and submitted to pressure of about 800 Mpa (8 t.cm^{-2}) [31]. The spectrum was recorded between 4000 – 400 cm^{-1} (2.5 – 15.4 µm) [31].

2.2.3.2. UV-Visible:

The CuO nanoparticles were dispersed in de-ionized water and then kept under ultrasonic vibration (35 Hz) to obtain a homogeneous mixture solution (0.1% Wt), which was used to determine and recording the absorption spectra using a UV spectrometer.

2.2.4. Determination of Thermophysical Properties of Nanofluids

2.2.4.1. Density:

The pychnometer was completely filled with the CuO/ water nanofluid, and then it was weighted by analytical balance. The density was calculated by equation:

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

2.2.4.2. Viscosity:

The controlled shear rate rheometer was applied to measure the viscosity of the CuO/ water nanofluids [32]. The rheological property of the nanofluids was measured by the viscometer with the thermostat, which controls temperature in the controlled shear rate rheometer.

The viscosity measurement was started at 20 ◦C, and temperature was gradually increased to 80 ◦C at an interval of 20 ◦C. The nanofluid temperature was also measured by using a thermocouple. All the viscosity measurements were recorded at steady state conditions.

Before the measurement of nanofluids, the viscometer was calibrated with the de-ionized water [32].

2.2.4.3. Specific heat capacity:

A heat-flux-type differential scanning calorimeter was used to measure the nanofluid specific heat capacities. The differential scanning calorimeter (DSC) measures the heat flux into a sample as a function of temperature during a user-prescribed heating regime. It accomplishes this by comparing the heat flux into a pan containing the sample with the heat flux into an empty pan.

Hermetically sealed aluminum pans (TA Instruments) were used in the tests presented here.

The classical three-step DSC procedure was followed to measure specific heat capacity. Additionally, testing procedures adhered to protocols set forth in the ASTM Standard Test Method for Determining Specific Heat Capacity by Differential Scanning Calorimetry. The three-step DSC procedure begins with designing a heating regime, which should contain the temperature range of interest. Next, a measurement is taken with two empty sample pans loaded into the DSC. During this measurement, the baseline heat flux, Q_0, is obtained. The results of this measurement indicate the bias in the machine, allowing for it to be accounted for during data reduction.

The second measurement is of a reference sample, with a known specific heat, cp,ref. A pan containing the reference sample and an empty pan are loaded into the DSC. The heat flux into the reference sample, Q_{ref}, is recorded throughout the identical heating regime.

The third measurement is made on the actual sample of interest. A pan containing the sample and an empty pan are loaded into the DSC. The heat flux into the sample, Q_{sample}, is recorded during an identical heating regime as the previous two measurements. The heat flux curves from the three measurements are used to comparatively determine the specific heat of the sample, cp,sample, where:

$$C_{p,sample} = \frac{Q_{sample} - Q_0\ M_{ref}}{Q_{ref} - Q_0\ M_{sample}}\ C_{p,ref}$$

And M_{ref} and M_{sample} represent the masses of the reference and sample, respectively. Sample masses were measured using a Perkin Elmer AD6 autobalance. In these tests, de-ionized water was used as the reference sample, with specific heat values obtained from Perry's Chemical Engineers Handbook.

The DSC heating procedure consisted of three steps:
(1) Equilibrate and remain isothermal at 25◦C for one minute,
(2) Ramp to 75◦C at 10◦C/min,
(3) remain isothermal at 75◦C for one minute.
Heat flux measurement was continuous from 25◦C to 75◦C. However, for analysis, specific heat capacity was calculated at 35◦C [33].

2.2.4.4. Thermal Conductivity:

Thermal conductivity of the CuO/water nanofluids is measured by using the thermal conductivity apparatus. The experimental setup consists of test section which is a metallic tube has a cylinder shape, length 235 mm, internal diameter 25mm, thickness 2-3 mm. The cylindrical tube was cooled by continuous supply of cooling water at a rate of 3 liters/min (condenser was used) in one of the end of the cylindrical tube. The other end is heated by graduated hot plate.

The temperatures of the fluid in the test section were measured by thermometer that placed in cretin points. The time of temperature measurement was recorded.

Conduction through cylindrical tube can be calculated from the internal radius, r_1, the external radius, r_2, the length,l, and the temperature difference between the inner and outer wall,T_2-T_1 .

The surface area of the cylinder is $Ar = 2\pi rl$

Thermal conductivity was determined by Fourier's low:

$$Q = -kAr\frac{dT}{dr} = -2k\pi rl\frac{dT}{dr}$$

$Q \equiv$ is the heat flow rate by conduction (W).
$k \equiv$ is the thermal conductivity of body material ($W \cdot m^{-1} \cdot K^{-1}$).
$A \equiv$ is the cross-sectional area normal to direction of heat flow (m^2) and
$dT/dx\equiv$ is the temperature gradient ($K \cdot m^{-1}$).

2.2.5. Stability test:

Stability test of copper oxide nanofluid has been done manually. The prepared Nanofluid was kept undisturbed for 50 days and the observable changes were recorded.

Chapter Three

Results and Discussion

Chapter three

3. Results and Discussions

3.1. Characterization of Copper Oxide Nanoparticles:
3.1.1. FT – IR Spectroscopy:

The spectrum has absorption bands at about 3400 cm^{-1} and 1625 cm^{-1} were due to the stretching and bending vibrations of –OH group.

The three beaks at (600 – 522 – 437) cm^{-1} are Cu-O stretching.

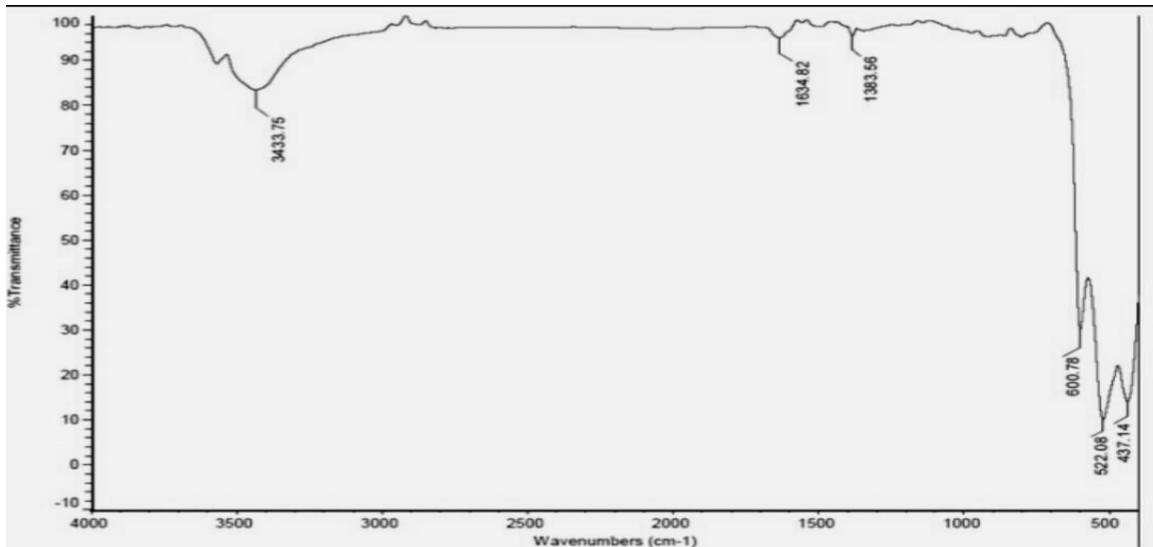
Figure (3.1): IR spectrum of Copper Oxide nanoparticles

3.1.2 UV-Visible:

The absorption spectra were used to study the energy band and the type of electronic transitions. Absorption spectra of CuO nanoparticles are shown in Fig. (3.2), which show a strong fundamental absorption, edge approximately 230 nm due to direct transition of electrons.
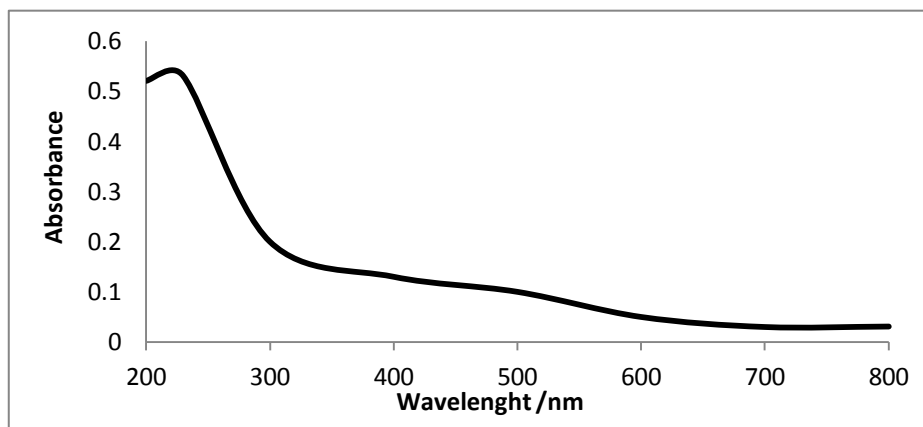

Figure (3.2): UV-Visible spectra for copper oxide/water nanofluid

3.2. Thermophysical Properties of Nanofluids:

3.2.1. Density:

From the experiment results, Density was found to increases by increasing the particle volume concentration of nanofluids at constant temperature (27℃).

Table (3.1): Density of copper oxide/water nanofluid at 27℃

Wt %	Vol %	Density at 27℃ , Kg/m3
De-ionized water	-	996.5
1	0.16	1002.4
2	0.32	1008.3
3	0.47	1013.7
5	0.79	1021.1

3.2.2. Viscosity:

From the experimental results, Viscosity was found to decreases with increases in temperature. As temperature increases, the average speed of the molecules in the nanofluid increases and the amount of time the nanoparticles dispersed in the base fluid spend "in contact" with their nearest neighbors decreases. Thus, as temperature increases, the average intermolecular forces decrease in between the nanoparticles.

That property is also depending upon the nanoparticle volume concentration present in the base fluid. Viscosity increases by increasing the particle volume concentration of nanofluids.

De-ionized water viscosity at 20 °C about 1.002 (mPa.s)

Table (3.2): Viscosity of copper oxide/water nanofluid at different temperatures for 1%, 2%, 3% and 5% CuO

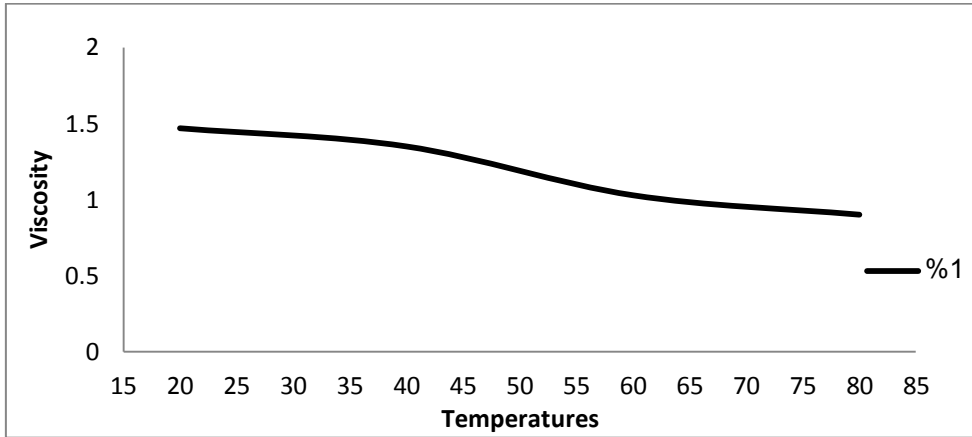| Temperature, °C	Viscosity, mPa.s			
	1%	2%	3%	5%
20	1.4686	1.4687	1.4690	1.4697
40	1.3495	1.3447	1.3530	1.3476
60	1.0296	1.0326	1.0390	1.0366
80	0.9024	0.9137	0.915	0.9169

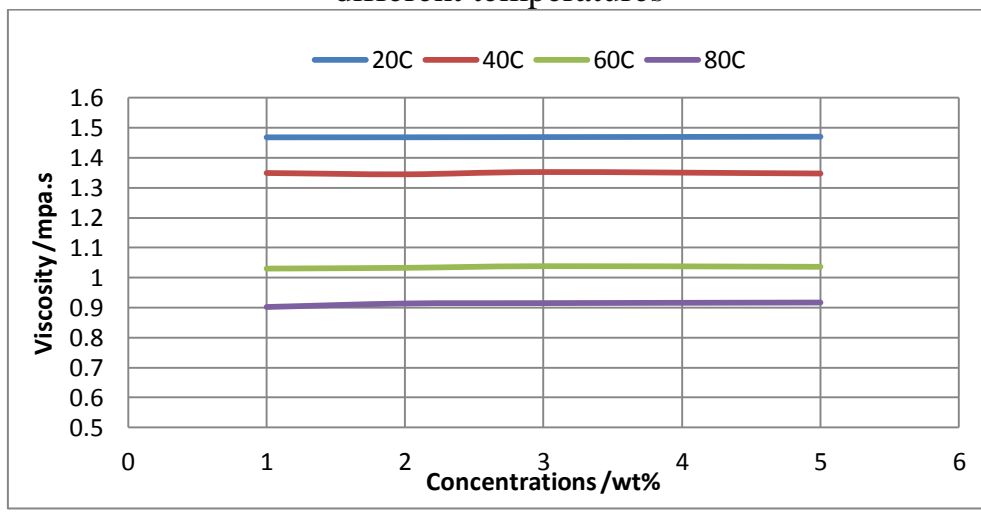Figure (3.3): Viscosities of 1% Wt copper oxide/water nanofluid in different temperatures

Figure (3.4): Viscosities of 1%, 2%, 3% and 5% Wt copper oxide/water nanofluid in different temperatures

3.2.3. Specific heat capacity:

Specific heat capacity of De-ionized water 4182 J/kg.K
The nanofluid specific heat is lower than the values of de-ionized water.
The specific heat of nanofluid decreases with the increase in concentration.

Table (3.3): Specific heat capacity of copper oxide/water nanofluid

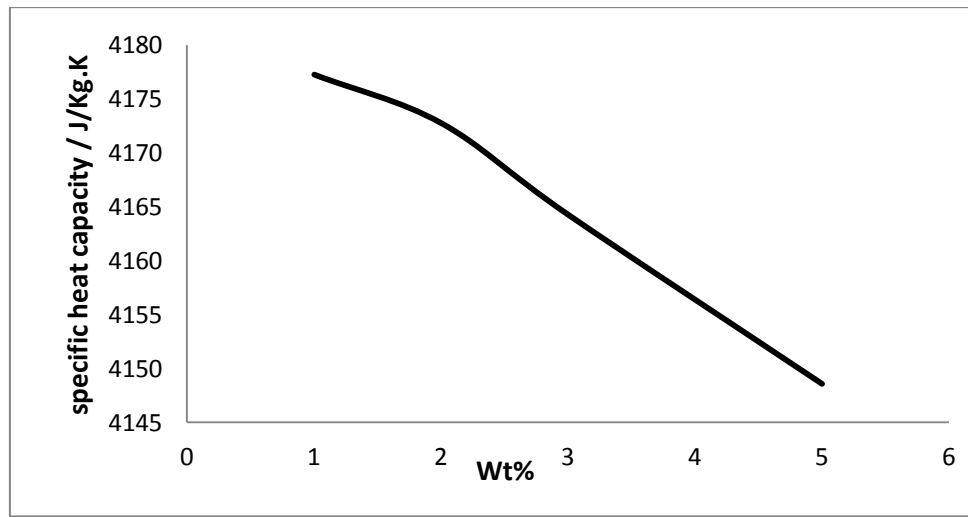| Wt %	Vol %	Specific heat capacity J/kg.K at 35℃
1	0.16	4177.3
2	0.32	4172.8
3	0.47	4164.3
5	0.79	4148.6

Figure (3.5): specific heat capacity of copper oxide/water nanofluid in different concentrations at 35℃

3.2.4. Thermal conductivity:

The experimental results show that a dramatic increase in the enhancement of thermal conductivity of CuO. This is due to the fact that as the temperature increases, the rate at which CuO particles moving in the nanofluid increases. The energy of motion of the nanoparticles increases with temperature and hence the rate at which heat is transferred in the nanofluid also increases.

The thermal conductivity of water 0.601 (W/m.K) at 25℃

Table (3.4): Thermal conductivity of copper oxide/water nanofluid

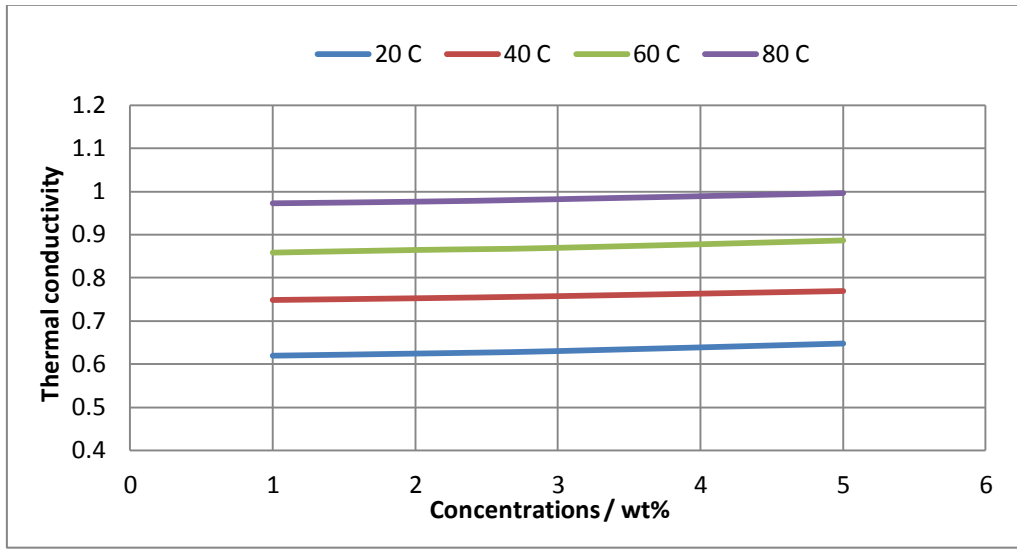| Temperature, °C	Thermal conductivity (W/m.K)			
	1%	2%	3%	5%
20	0.619	0.624	0.630	0.648
40	0.749	0.753	0.758	0.770
60	0.858	0.864	0.869	0.886
80	0.972	0.976	0.982	0.997

Figure (3.6): Thermal conductivity of copper oxide/water nanofluid in different concentrations at different temperatures

3.3. Stability test:

During first 20 days it has been found that there is no physical change observed in nanofluid. Some amount of nanoparticle has been settled after 50 days has been observed. This may be because of high density of copper nanoparticle .Ideal nanofluid can been obtained when the nanofluid is stable for long period of times.

Figure (3.7): Sedimentation test of Copper Oxide nanofluid.

3.4. Conclusion:

- The copper oxide nanofluid has been successfully synthesized in two steps, ultrasonic vibrations was used for depressing nanoparticles into fluid to uniform the prepared nanofluid of different concentrations.

- Characterization of copper oxide nanoparticles by UV /Visible and FT-IR spectroscopy.

- At constant temperature, density and viscosity were found to increase by increasing the particle volume concentration of nanofluids.

- The specific heat of nanofluid decreases with the increase in concentration.

- Increase in the amount of copper nanoparticles increases the thermal conductivity of the fluid up to a certain value of volume fraction of CuO.

- The stability of nanofluid was measured using sedimentation method. It was found that nanofluids are stable for approximately 25 days. After 50 days light settlement was observed this may be due to the particle density.

- It could be concluded that the copper oxide nanofluids prepared can be effectively used as coolants for automobile and heat transfer applications.

3.5. Recommendations:

– Copper oxide nanopowder can be mixed with other metal oxide such as Aluminum oxide in different ratio and it will give new thermophysical properties values.

– More accurate values of thermal conductivity can be obtained by using KD2 Pro instrument.

– Further characterization of the copper (II) oxide nanopowder can be obtained with TEM , SEM and XRD

References:

1. Batista, C.A.S., Larson, R.G. and Kotov, N.A., **2015**. Nonadditivity of nanoparticle interactions. *Science*, *350*(6257), p.1242477.

2. Das, S.K., Choi, S.U., Yu, W. and Pradeep, T., **2007**. *Nanofluids: science and technology*. John Wiley & Sons.

3. Wen, D., Lin, G., Vafaei, S. and Zhang, K., **2009**. Review of nanofluids for heat transfer applications. *Particuology*, *7*(2), pp.141-150.

4. Manna, I., **2012**. Synthesis, characterization and application of nanofluid—an overview. *Journal of the Indian Institute of Science*, *89*(1), pp.21-33.

5. Ebrahimi, S., Gavili, A., Lajevardi, M., Isfahani, T.D., Hadi, I. and Sabbaghzadeh, J., **2010**. New Class of Coolants: Nanofluids. In *Cutting Edge Nanotechnology*. InTech.

6. Wang, X.Q. and Mujumdar, A.S., **2008**. A review on nanofluids-part I: theoretical and numerical investigations. *Brazilian Journal of Chemical Engineering*, *25*(4), pp.613-630.

7. Klabunde, K.J. and Sergeev, G.B., **2013**. *Nanochemistry*. Newnes

8. Yu, W., Xie, H. and Chen, L., **2012**. Nanofluids. In *Smart nanoparticles technology*. InTech.

9. Heyd, R., **2011**. Nanofluids for Heat Transfer. In *Two Phase Flow, Phase Change and Numerical Modeling*. InTech.

10. Joulain, K., Carminati, R., Mulet, J.P. and Greffet, J.J., **2003**. Definition and measurement of the local density of electromagnetic states close to an interface. *Physical Review B*, *68*(24), p.245405.

11. Vajjha, R.S., Das, D.K. and Mahagaonkar, B.M., **2009**. Density measurement of different nanofluids and their comparison with theory. *Petroleum Science and Technology*, *27*(6), pp.612-624

12. Sharma, K.V., Suleiman, A., Hassan, H.S.B. and Hegde, G., **2017**. Considerations on the Thermophysical Properties of Nanofluids. In *Engineering Applications of Nanotechnology* (pp. 33-70). Springer, Cham.

13. Maheshwar, M., A REVIEW ARTICLE ON MEASUREMENT OF VISCOSITY.

14. Halliday, D., Resnick, R. and Walker, J., **2010**. *Fundamentals of Physics, Chapters 33-37*. John Wiley & Sons.

15. Kittel, C., **2005**. Introduction to Solid State Physics. *University of Pennsylvania Law Review*, *154*(3), p.477.

16. Perry, R.H. and Green, D.W., **1997**. Perry's Chemical Engineers' Handbook (ed.). *Seventh, International edition*.

17. Phiwdang, K., Suphankij, S., Mekprasart, W. and Pecharapa, W., **2013**. Synthesis of CuO nanoparticles by precipitation method using different precursors. *Energy Procedia*, *34*, pp.740-745.

18. Sarojini, K.K., Manoj, S.V., Singh, P.K., Pradeep, T. and Das, S.K., **2013**. Electrical conductivity of ceramic and metallic nanofluids. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *417*, pp.39-46.

19. Warrier, P. and Teja, A., **2011**. Effect of particle size on the thermal conductivity of nanofluids containing metallic nanoparticles. *Nanoscale research letters*, *6*(1), p.247.

20. Kulkarni, D.P., Vajjha, R.S., Das, D.K. and Oliva, D., **2008**. Application of aluminum oxide nanofluids in diesel electric generator as jacket water coolant. *Applied Thermal Engineering*, *28*(14-15), pp.1774-1781.

21. Ganguly, S., Sikdar, S. and Basu, S., **2009**. Experimental investigation of the effective electrical conductivity of aluminum oxide nanofluids. *Powder Technology*, *196*(3), pp.326-330.

22. Pantzali, M.N., Mouza, A.A. and Paras, S.V., **2009**. Investigating the efficacy of nanofluids as coolants in plate heat exchangers (PHE). *Chemical Engineering Science*, *64*(14), pp.3290-3300.

23. Philip, J. and Shima, P.D., **2012**. Thermal properties of nanofluids. *Advances in Colloid and Interface Science*, *183*, pp.30-45.

24. Zhu, H.T., Lin, Y.S. and Yin, Y.S., **2004**. A novel one-step chemical method for preparation of copper nanofluids. *Journal of colloid and interface science*, *277*(1), pp.100-103.

25. Wen, D., Lin, G., Vafaei, S. and Zhang, K., **2009**. Review of nanofluids for heat transfer applications. *Particuology*, *7*(2), pp.141-150.

26. Nikkam, N., Ghanbarpour, M., Saleemi, M., Haghighi, E.B., Khodabandeh, R., Muhammed, M., Palm, B. and Toprak, M.S., **2014**. Experimental investigation on thermo-physical properties of copper/diethylene glycol nanofluids fabricated via microwave-assisted route. *Applied Thermal Engineering*, *65*(1-2), pp.158-165.

27. Wang, X.J., Li, X.F., Xu, Y.H. and Zhu, D.S., **2014**. Thermal energy storage characteristics of Cu–H2O nanofluids. *Energy*, *78*, pp.212-217.

28. Lu, L., Lv, L.C. and Liu, Z.H., **2011**. Application of Cu-water and Cu-ethanol nanofluids in a small flat capillary pumped loop. *Thermochimica acta*, *512*(1-2), pp.98-104.

29. Philip, J. and Shima, P.D., **2012**. Thermal properties of nanofluids. *Advances in Colloid and Interface Science*, *183*, pp.30-45.

30. Lavernia, E.J. and Srivatsan, T.S., **2010**. The rapid solidification processing of materials: science, principles, technology, advances, and applications. *Journal of Materials Science*, *45*(2), p.287.

31. Shah, P.B. and Patel, P.U., **2012**. Q-absorbance ratio spectrophotometric method for the simultaneous estimation of cinnarizine and dimenhydrinate in their combined dosage form. *J. Pharm Sci and Bio-scientific Res*, *2*(2), pp.83-87.

32. Duan, F., **2012**. Thermal property measurement of AL2O3-water nanofluids. In *Smart nanoparticles technology*. InTech.

33. O'Hanley, H., Buongiorno, J., McKrell, T. and Hu, L.W., **2012**. Measurement and model validation of nanofluid specific heat capacity with differential scanning calorimetry. *Advances in Mechanical Engineering*, *4*, p.181079.