

Nanofluids: A Review Preparation, Stability, Properties and Applications

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Abstract—Nanofluids, suspension of nano sized particles having higher conductivity than base fluid, has reported many interesting properties which gains the attention of researchers and proved vital in many applications. This document is a review article on nanofluids. The article provides the basic information about nanofluids, their preparation methods, stability analyses, thermophysical properties and applications. Also discusses the future scope of nanofluids.

Keywords—nanofluids; nanofluids preparation; stability; thermophysical properties;

I. INTRODUCTION

With the advancement in microelectronics industry, high heat flux devices has been started manufactured, but their heat dissipation is critical issue for their prominent use in industry and day to day life, since electronic chips slows down their functioning or even may damage completely due to heat accumulation. Hence the heat dissipation from these electronic chips and circuitry is most important and challenging task. However, the conventional coolants (water, oils and ethylene glycols) were proved futile because of their low thermal conductivity which leads to poor heat dissipation and slower performance of electronics chips. Therefore in 1873, J.C Maxwell proposed to add very small solid particles in the fluids (base fluids) to increase their thermal conductivity which further can increase the heat dissipation capacity. Small solid particles have higher thermal conductivity than base fluid hence an overall increase in heat dissipation capacity and thermal conductivity of base fluid [1].

It is known that micro and millimeter sized particles increases the thermal conductivity of base fluids, but when experiments were carried out it was found that in addition to increase in thermal conductivity some more problems like abrasive wear of pipeline, clogging of channels, sedimentation of particles and pressure drop, has been surfaced which restrict their use in micro industry. Later, to avoid these problem nano sized particles were introduced; with the development in nano scale industry and nanotechnology they gained the momentum for use in research area [2]. Nano particles are fine powdered particles which have size smaller than 100 nm. In 1993 Masuda et al [3] used the ultra-fine particles to enhance the thermal

conductivity of liquid. Later in 1995, S.U.S Choi [4] proposed the use of nanoparticles in base fluids to increase the thermal conductivity. These particles may be metallic and non-metallic: Al_2O_3 , CuO, SiO_2 , TiO_2 , Cu, Ni, Al, ZnO [5]. The fluid made by dispersing nanoparticles in them is known as nanofluids [5]. Nanofluids are the class of fluids which are formed by dispersing nano sized high conductivity materials (nanofibers, nanotubes, nanorods, nanowires, nanoparticles or nanosheets) into the base fluid, generally water, oils, ethylene glycol. The dilute suspensions of nanofluids are the advantage over colloidal solution for being having high heat transfer surface between fluid and particles. With these advantages nanofluids have applications in : transportation, heat transfer intensification, electronics applications, industrial cooling applications, heating buildings and reducing pollution, nuclear cooling, energy storage, solar absorption, friction reduction, magnetic sealing, biomedical application, nano drug delivery etc. [6]. There is two phase system in nanofluids one is solid and other liquid phase. Nanofluids possess better thermal properties (thermal conductivity, thermal diffusivity, convective heat transfer coefficient) than the base fluids. However with enhanced properties, in two phase system stability is the major challenge before the researchers. In this paper we will discuss preparation methods, some stability methods, thermophysical properties and applications of nanofluids.

II. PREPARATION OF NANOFLUIDS

A. Two- step method

It is the most widely used method for preparing nanofluids, nanotubes, nanosheets and other nanomaterials. In this method nanoparticles are first made in dry powdered by different means of physical and chemical processes and then these nanoparticles are dispersed in base fluid with the help of ultrasonic agitation, ball milling, homogenizing, magnetic force agitation . This method is economic and easy way to produce nanofluids on large scale because nanotechnology industry has grown to these scales to produce these particles economically. However due to high surface activity nanoparticles made by this method has the tendency to agglomerate. The major steps in preparing nanofluids are given as. 1) Amount of nanoparticles required; calculated and weighed by using highly accurate and precise weighing machine. 2) After knowing the exact quantity of nanofluids,

corresponding quantity of base fluid is to be taken in beaker and kept on magnetic stirrer with magnetic bead rotating inside it. Nanoparticles are to be poured very slowly in very less quantity in steps in the base fluid while the magnetic stirrer is on. They have to be stirred on magnetic stirrer for 20 minutes. The pouring of nanofluids in base fluids and the temperature of magnetic stirrer plate are the major concerns while stirring. 3) After stirring the solution has to be sonicated for almost 80- 100 minutes in ultrasonic vibrator. Proper sonication is required for better stability of nanofluids; however pouring of nanofluids in base fluid impacts the stability. For increasing the stability of nanofluids surfactants can be used but functionality of surfactants at higher temperatures is also a big problem. Due to the stability issues with two step method several other methods have been developed, including one step method. In the following part we will discuss one step method

B. One-step method

To reduce the problem of agglomeration, in 2007 Eastman et al. developed the one step vapor condensation method to prepare Cu/ethylene glycol solution of nanofluids [7]. One step method is simultaneous making and dispersion of nanofluids. In this method nanofluids are directly synthesized in base fluid thus storage, transportation, pouring, mixing and drying of nanoparticles are avoided, which increases the stability of nanofluids and agglomeration is reduced by many times [8]. Vacuum submerged arc nanoparticle synthesis system is also another efficient method to prepare nanofluids by one-step method [9].

One-step method cannot synthesize nanofluids in large scale due to heavy cost involvement in it, one-step chemical method is developing very rapidly which can make preparation of nanofluids by one-step method economical in near future. In 2004, Zhu et al presented the new method to prepare copper nanofluids by reducing $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ with $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ in ethylene glycol in microwave irradiation [10]. Silver nanofluids with mineral oil as base fluids were also prepared by this method. However, one step method has some critical disadvantages. The most important is the residual of reaction was left behind in nanofluids and it is difficult to remove the residual from the solution. The thermal properties are difficult to predict exactly with these impurities. The main advantage of one step method is the stability it gives and the structure of nanoparticles can be controlled by varying the synthesis parameters.

III. NANOFUIDS: STABILITY AND PROPERTIES

The aggregation and agglomeration of nanoparticles creates hindrances in the flow path in microchannels or may even clog the channels, increase in size of particles also decrease the thermal conductivity of nanofluids. Hence stability becomes the key issue which influences the application and utility of nanofluids. In following section we will discuss 1) the stability evaluation method, 2) ways to enhance stability, 3) stability mechanism

A. Stability evaluation methods

a) *Sedimentation and centrifugation method.* Sedimentation is the most simple method to evaluate the stability of nanofluids [11]. The sediment weight or volume under external forces is the measure of stability of nanofluids.

The nanofluids is said to be constant when the concentration or particle size remains constant with time and space. Special cameras can be used to photograph the sediment at the base of the fluid. Sediments on sedimentation tray were weighed and particle volume fraction of solution was measured for a particular time. This method shows the change in fraction and the sediments in particular time period. However the longer time period for observation in this method causes error. Therefore centrifugation method was developed to evaluate the stability of nanofluids. In this method solution is made to centrifuge at particular rpm to check the stability of nanofluids. Singh et al centrifuged the silver nanoparticles at 3000 rpm for 10 hours with no sedimentation at the end, this shows the particles were stable in solution.

b) *Zeta Potential Measurement.* Zeta potential is the electric potential of double interfacial layer at the surface of dispersed particle at the slipping plane to the point in bulk fluid away from interface, the significance of this electric potential is that its value is related to the stability of nanofluids. It is known that the nanofluids with higher zeta potential have higher stability and nanofluids with lower zeta potential have lower stability. Generally zeta potential value from 40-60 mV is considered as stable, whereas zeta potential value with 60 mV and above is considered as highly stable. Zeta potential method measures the potential difference between stationary layer of fluid particle and dispersion medium. However 25 mV is taken arbitrarily value to distinguish between low charge surfaces and high charge surfaces which distinguishes between low stability and high stability nanofluids. Kim et al [12] checked the stability of silver nanofluids and found nanofluids stable even after a month this is due to high negative zeta potential of silver nanofluids. Zhu et al [13] checked the zeta potential of $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ with different pH values.

c) *Spectral Absorbency Measure.* It is the another efficient method for measurement of stability of nanofluids. In general there is direct relation between concentration of nanofluids and absorbency intensity. The variation in supernatant particle in the solution with time is obtained by measurement of absorbency of UV by nanofluids. The excellent advantage of this method is that it provides the quantitative measurement of stability of nanofluids with time. The nanofluids concentration is measured by degree of absorbency of UV-vis spectral by nanofluids, more is the absorbency more is stability of nanofluids. Chen and Xie [15] measured the stability of multi walled nanotubes (MWNT) by UV-vis absorption spectra at different concentrations.

B. Stability Enhancement Methods

a) *Surfactants.* Surfactants in nanofluids are also called dispersants. Dispersants affects the surface characteristics of nanofluids in small quantity. Dispersants have two parts in it one is head and another is tail. Head is hydrophilic and tail is hydrophobic (long carbon chain) part of dispersant. Dispersants act as contact enhancer between two phases (solid and liquid). In nanofluids dispersants are located the interface of particle and fluid and they form the continuity in two phases and binds the particles with base fluid medium, in this way they increases the stability of nanofluids [6].

Depending on the composition of head, surfactants are divided in to four groups as described by Yu and Xie: 1) If head is without charge it is known as nonionic surfactant e.g.

Alcohols, 2) anionic surfactant if head is negatively charged e.g. Alkyl sulfates, 3) if head is positively charged then it is cationic surfactants, 4) amphoteric surfactants zwitterionic head. The major issue in using the surfactants is how to choose them. Generally when base fluid is polar solvent we use water soluble surfactants otherwise use oil soluble surfactants. With nonionic surfactants hydrophilic/lipophilic balance (HLB) value is to be checked. HLB value can be found from any handbook. More the HLB value is more oil soluble surfactant is, lesser the HLB value is more the water soluble surfactant is. With these advantages, surfactants have associated problem with them. Surfactants may contaminate the nanofluids solution by making foam during heating. Surfactants molecules get attach to the nanoparticles which impacts the thermal conductivity of nanofluids [14]. Thermal capacity of nanofluids decreases with addition of surfactants in them.

b) Surface modification techniques. This is a surfactant free technique, aims to achieve higher stability with no or minimum compromise with thermal conductivity of nanofluids. The surface of nanoparticles is modified by using chemicals. Mechanochemical techniques make the particles more stable in base fluid solution. Chen et al [15] used mechanochemical technique to prepare single and double layered carbon nanotubes (CNTs). The stability was checked by zeta potential and infrared spectrum techniques and it was found that hydroxyl group gets attached to the surface of CNTs, which makes them stable in corresponding base fluid. Yu et al [16] modified the surface of diamond by giving plasma treatment. Tang et al [17] modified zinc oxide nanoparticles with polymethacrylic acid (PMMA) in aqueous solution. The carboxyl group of PMMA interacts with zinc surface and form poly complex. The modification did not have any impact on crystalline structure of zinc oxide nanoparticles. In this way the technique can be developed easily to make the nanoparticles more stable without any additives and surfactants.

c) Stability Mechanism. In dispersion the particles adhere to each other and form agglomerates of increasing size, which further settles down and clogs the passages of microchannels; hence questions the credibility of nanofluids in practical applications. According to Derjaguin, Verwey, Landau, and Overbeek (DVLO) the stability of particle is determined by sum of electrical double layer repulsive force and van der Waal forces between the particles which arises due to their Brownian motion. When the van der Waal forces dominant over the electrical repulsive forces particle stick to each other and form agglomerates, when the electrical repulsive forces are more than van der Waal forces particles do not get aggregated and good stability characteristics are observed. So, for stability of nanofluids the electric repulsive forces should be more than the van der Waal forces. These forces can be modified by adding surfactants and additives and the stability can be enhanced, for e.g. Zinc oxide nanoparticles with PMAA shows good compatibility with polar solvents. Surfactants and reagents increase the stability of nanofluids for more duration but they also affect the thermal properties of nanofluids. They should be used in metered and limited quantity. Kamiya et al [18] studied the behavior of dense alumina structure and effect of polymer dispersant structure on electrostatic interaction and obtained

an optimum ratio of hydrophilic to hydrophobic group for maximum force and minimum viscosity.

C. Thermophysical properties of nanofluids.

In 1873, J.C. Maxwell proposed the addition of small metallic particles in fluids to increase the thermal conductivity of suspensions [1]. From then researchers showed a great interest in thermophysical properties of nanofluids [7, 13, 19-25]. The thermophysical properties of nanofluids includes: density, thermal conductivity, viscosity, specific heat.

a) Density: Is the ratio of mass per unit volume. On adding the high conducting nanoparticles in base fluids the density increases, because of insertion of particles in same volume. The density can be calculated by using the commonly used formula given in [26]. Density does not show the larger effects in with small concentrations. Wu et al [27] measured the density of $\text{Al}_2\text{O}_3\text{-H}_2\text{O}$ nanofluids of 0.15% and 0.26% particle volume concentration at 27.5°C and found out to be 1002.2 and 1003.1 kg/m^3 respectively. Salman et al [5] noted the density of SiO_2 nanofluids with 0.5% and 1% concentration by volume, found out to be 1003 and 1010 kg/m^3 respectively. With insertion of nanoparticles in base fluids they become thicker which in turn affects the viscosity of nanofluids. Density does not get effected for small concentrations upto 0.5 % (vol).

b) Viscosity: Very few work has been done on viscosity in addition to other thermophysical properties [28-31]. The influence of concentration and temperature was investigated by these works. However, the viscosity of nanofluids greatly depend on the degree of agglomeration of nanoparticles and difference in results of various literatures can be found depending upon particle size, shape, ionic strength, pH value of the medium [2]. There exist formulas which predict the viscosity of nanofluids [32]. Li et al [33] investigated the apparent viscosity of $\text{CuO-H}_2\text{O}$ nanofluids and results showed that there is decrease in viscosity with increase in temperature and increase in viscosity with increase in concentration. Wu et al [27], Kamaldeep et al [34] also found the similar results with $\text{Al}_2\text{O}_3\text{-H}_2\text{O}$ nanofluids. In 1956, Einstein first gave the model for prediction of viscosity [2]. Hence it can be said that viscosity of nanofluids decreases with increase in temperature and increases with increase in particle volume concentrations. However, viscosity of nanofluids can be easily determined by viscometer. Temperature variation of viscosity also be studied with viscometer. Viscometer measures viscosity by rotating spindle in fluid. The concept of two cylinders is used in viscometer with inner rotating cylinder and stationary outer cylinder, the gap between cylinders is filled with nanofluids. The torque required by the spindle to rotate is calculated and by calibrated spring which is connected to rotary transducer measures the viscous drag. Ostwald viscometer, also known as glass capillary viscometer, is a u-tube arrangement which has two bulbs at two arms of viscometer, in one bulb the fluid is drawn and then allowed to pass to another bulb. The time taken by the liquid to pass to another bulb upto a specified mark is proportional to the viscosity. From the two methods discussed here viscosity can be measured easily.

c) Thermal conductivity: From the available literature it has been noticed that thermal conductivity is the most studied property of nanofluids [21, 22, 28, 34-40]. Pak and Cho [41]

and Eastman et al [42] studied the effect on thermal conductivity of $\text{Al}_2\text{O}_3\text{-H}_2\text{O}$ and alumina-ethylene glycol and found the increment in thermal conductivity of nanofluids than the base fluid. Kamaldeep et al [34], Das et al [43] investigated the effect of temperature on thermal conductivity of nanofluids and an increase in thermal conductivity with increase in temperature has been found. Due to presence of higher conductivity nanoparticles the thermal conductivity of nanofluids gets increased. Hence, it can be said that particle concentration and temperature increase has increasing effect on thermal conductivity of nanofluids. Many researchers have given the thermal conductivity model details of which can be studied in Mondragon et al [2]. Maxwell gave the equation which applies to smaller particle concentrations [1] and is most widely used equation for theoretical calculation of thermal viscosity.

Apart from the theoretical predictions thermal conductivity can be measured with KD2 Pro conductimeter, Decagon Devices Inc. KD2 Pro is the commercial device which measures the conductivity of fluids by using transient hot wire technique. A thin metallic wire is immersed in fluid which act as both heat source and temperature sensor. The temperature/time response is measured in transient hot wire technique. The test sample is poured in its glass tube, then sensor needle is to be inserted in this glass tube. It is very important to ensure the vertical position of sensor needle, to minimize the convective heat transfer effects inside the glass tube. To carry out measurement at high temperatures the glass tube is inserted in thermostatic bath where temperature is controlled digitally. To reduce the free convection inside the tube it is to be taken care for the temperature difference of sensor needle temperature and fluid inside the tube should be minimum. KD2 Pro uses special algorithms to examine the measurements during a cooling and a heating interval. This device is specially designed to measure the thermal conductivity of solids and liquids where temperatures are not affected by external disturbances.

d) Specific heat: The specific heat of nanofluids can be measured in Differential Scanning Calorimeter (DSC). Very less work is available on specific heat and its behavior with temperature. DSC analyses the heat capacity (Cp) of fluid according the variation in temperature. A sample of known mass is heated or cooled and its variation in heat capacity is tracked [44]. Kamaldeep et al [34] studied the effect of concentration on specific heat of $\text{Al}_2\text{O}_3\text{-H}_2\text{O}$ nanofluids. The results show the decrease in specific heat of nanofluids with increase in particle volume concentration. This is due to the fact that nanoparticles have lesser heat capacity than pure water. Due to mixing of lower heat capacity particles the overall heat capacity goes down.

IV. APPLICATIONS

a) Electronic applications: Due to higher heat generation in chips, electronic circuitry components with compact designs and geometry suffering from thermal management. To extract such a high heat from these compact devices has become difficult. Heat can be removed by two methods: by optimizing the design of cooling system and other by using high heat dissipating capacity fluids. Here nanofluids play the role of higher heat carrying capacity fluids than conventional coolants. Nanofluids have higher thermal conductivity

compared to those of base fluids, as proved by many researchers.

b) Transportation: Nanofluids have the capacity to advance the cooling systems of heavy duty engines and heat generating parts of automobiles. Nanofluids increase the heat carrying rate and thus lower the weight and reducing the complexity of cooling jackets. This helps in creating compact designs for same horse power with lighter radiators. It is beneficial for high performance and high fuel economy.

c) Heating buildings and reducing pollution: Kulkarni et al [23] evaluated heating of buildings in cold region with the help of nanofluids. In colder regions ethylene glycol mixed water in different proportions is used as heat transfer fluid. The analysis by Kulkarni et al [23] showed that by using nanofluids in heat exchanger, could reduce the mass and volumetric flow rates, which results in overall saving in pumping power. Nanofluids call for smaller and compact heating systems, which are capable of delivering the same amount of energy as larger systems.

d) Nuclear cooling systems: Researchers at Massachusetts Institute of Technology are exploring the applications of nanofluids in nuclear science. They are mainly focused in three areas: 1) Main reactor pressurized water reactors (PWRs). 2) As a coolant for emergency condition for core cooling. 3) Coolant for in vessel retention of the molten core during severe accidents in high-power-density light water reactors [45].

e) Space and Defense: The restriction of space, energy and weight at space stations and in aircraft generates the need for highly efficient cooling system which have high heat flux capacity. This presenting a vision for lighter weight of cooling systems due to compact and simple designs of heat exchangers, which further makes space travel cheaper than present. The high critical heat flux capacity make nanofluids capable of being used in military systems such as in submarines, high power diode lasers etc. thus nanofluids has the potential to be used in the areas where components should be lighter weight and power density is more.

f) Solar absorption: Solar energy is the best non-conventional source of energy available in abundance. Direct absorption solar collector is well established technology. But the efficiency is very low due to poor absorption capacity of collector fluid. Recently this technology has been pooled with nanofluidic technology. Otanicar et al [24] performed experiments on direct absorption solar collector with nanofluids as working fluid and reported 5% increase in efficiency of solar thermal collectors.

g) Miscellaneous: Along with these major applications of nanofluids, they have much more application in different fields for e.g. Nanodrug delivery, in microreactors, as vehicular brake fluids, nanofluids based microbial fuel cell, magnetic sealing, friction reduction etc.

V. FUTURE SCOPE

Nanofluids have shown great potential in many applications. But still its commercialization is facing many hindrances which are as discussed here. Firstly, due to the lack of agreement on results by many researchers created a need for further study and experimentation to find out the factors causing difference in results. Secondly, the stability of

the nanofluids suspensions is the key issue for research and practical applications. New methods and techniques should be developed to make nanofluids more stable without compromising on thermophysical properties of nanofluids. Thirdly, there is lack of investigation on nanofluids at higher temperatures, also at higher temperature dispersants degrade in their function or even form foam, hence higher temperature investigation is needed in view to upgrade nanofluids stability and surfactants behavior. Fourthly, higher concentrations increase the viscosity which requires more pumping powers. Lastly, nanofluids properties largely depend on the shape and size of additives. Thermal conductivity of nanofluids gets affected by degree of agglomeration of nanoparticles. Nanoparticles due to their utility in many applications are the future coolants with higher thermal conductivity.

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