Nanofluids Preparation and Stability for Heat Transfer Applications – A Review

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ABSTRACT
Miniaturized and highly efficient thermal systems represent the current requirements of the automobile, industrial as well as residential cooling and heating systems. But the performance of the modern thermal systems is primarily limited by the lower conductivity of the fluids being used in these systems. As a result of research and technology advancements, the concept of Nanofluids was introduced. The term Nanofluids broadly refers to the fluids with particles of average size less than 100 nm dispersed in it. The presence of these particles drastically alters the thermal and transport properties of the base fluid due to which there is a wide scope of their applications. This paper provides a summarized review of the current research in this field with main focus on preparation, stability and thermal properties of the Nanofluids.

Keywords
Nanofluids, nanoparticles, thermal conductivity, viscosity, density, specific heat, stability, heat transfer

1. INTRODUCTION
Primarily conventional fluids like water, lubricating oil and coolant additives like ethylene glycol etc. are employed as the working fluids for the heating and cooling systems. One of the major limiting factors for the low heat transfer performance of these fluids is their poor thermal conductivity. Hence the idea of dispersing solid particles in the fluid was introduced in order to improve the thermal conductivity of the fluid and thus improve their heat transferring characteristics. High conductivity of solids can be utilized in increasing the thermal conductivity of a fluid by the addition of small solid particles to the fluid. The feasibility and application of the usage of such mixtures of solid particles with sizes ranging from 10^{-9} to 10^{-7} meters was previously examined by many researchers.

Nanofluid is a new type of heat transfer fluid, having nanoparticles (1–100 nm) which are evenly distributed in the base fluid. These uniformly distributed nanoparticles are generally metal or metal oxides which have a great enhancing effect on the thermal conductivity of the nanofluid, thus increasing conduction and convection coefficients and allowing for higher heat transfer. Nanofluids are being examined for use as advanced heat transfer fluids for the last two decades. However, because of the complexity and variety of nanofluid systems, no particular agreement has been reached till now on the possible benefits of using these fluids for heating/cooling applications.

Nanofluid cannot be considered simple liquid-solid mixture. It is important to achieve agglomeration-free suspension for considerably long time periods without the possibility of any changes in chemical composition of the base fluid. This can only be achieved by reducing the density difference between liquids and solids or by increased viscosity of base fluid. For two-phase systems one of the major issues is the stability of these nanofluids, and till date it has remained a challenge. This paper will provide an insight into the advancements made in methods of preparation of stable nanofluids and try to summarize the mechanisms.

2. PREPARATION METHODS
The preparation of nanofluids from nanoparticles can be broadly categorized under the following two methods.

2.1 Two-Step Method
The Two-step method is the most commonly used method for preparing nanofluids. Nanoparticles, nanotubes (carbon nanotubes), nanofibers and other nanomaterials utilized in this method are produced as dry powders first by the means of chemical and physical methods. After that the powder is be dispersed into a base fluid in the second step, with the help of external mixing or stirring methods like magnetic agitators, ultrasonic agitators, high-shear mixers, homogenizing or ball milling. The Two-step method is the most commonly used and economic method to prepare nanofluids in large quantities because the nanopowder manufacturing techniques have already started providing up to required industrial production levels. Because of the high surface area and surface related activity, the nanoparticles have a tendency to accumulate together. One of the important methods to improve the stability of nanoparticles in base fluids is to use surfactants which reduce surface tension of base fluids.

2.2 One-Step Method
Because of the difficulties faced regarding stability during the mixing process in preparing nanofluids by Two-step method, the One-step method was developed. In order to reduce the accumulation of nanoparticles, Eastman et al. [2] suggested the one-step physical vapor condensation process for preparing Cu/ethylene glycol nanofluids. In this one-step method, it involves the simultaneous synthesis and dispersion of the nanoparticles in the base fluid. By this method, the drying, storage and transportation processes are removed, so the accumulation of nanoparticles is kept at a minimum. Thus the stability of fluids is greatly increased [1]. The one-step method can be used to prepare fluids with uniformly dispersed nanoparticles and these particles can be kept suspended in a stable manner. The nanoparticles so prepared have needle-like, square, polygonal or circular morphological shapes. The One step process avoids the unwanted particle aggregation quite well.

3. STABILITY ANALYSIS

The sticking together of particles termed as agglomeration leads to settlement of the dispersed particles. Prolonged agglomeration can result in large deposits of particles which can further result in clogging, especially in case of micro channels where the fluid passages are already very small. Hence stability is also an important factor that needs to be considered.

3.1. Methods for Evaluating Stability

3.1.1 Sedimentation method

This method is the simplest method for evaluation of stability [3]. An external force is utilized to initiate the sedimentation. The sediment weight or the sediment volume measured after the predetermined time period represents the stability. They are said to be stable if the dispersed particle concentration remains constant with respect to time. The sedimentation method was utilized by Zhu et al. [4] during experimentation in order to establish graphite suspension stability. Most researchers capture photographs of the samples at regular time intervals for 24 hours after the nanofluid sample is prepared to determine sedimentation and hence conclude its stability [5, 6]. The only drawback of sedimentation method is the long period for observation it requires. Therefore it can be expedited by the action of a centrifugal force by placing the sample in a setup to spin it at a speed of around 3000 rpm [7]. This improved method for sedimentation is termed as Centrifugation method.

3.1.2 Spectral analysis method

Spectral absorbency analysis is also an efficient method to study the stability of nanofluids. Generally the relationship between the absorbance intensity & concentration of particles in the fluid is linear. If the nanoparticles dispersed in the fluid have a characteristic absorption band in the region of 190–1100 nm wavelength, then it is a simple and reliable method to establish the stability of nanofluids. It utilizes UV-visual spectral analysis. Its advantage is that it gives quantitative results with respect to concentration of nanofluids [8].

3.1.3 Zeta Potential Analysis

Zeta potential is defined as the potential difference between dispersion fluid and the layer of stationary attached to the surface of the dispersed particles. It represents the degree of repulsion amongst similarly charged adjacent particles. The Zeta potential can be either positive or negative. Therefore suspensions with a high value of zeta potential are considered to be electrically more stable as compared to suspensions with low zeta potentials. The values of zeta potential ranging from 40-60 mV are believed to be highly stable. Kim et al. [9] performed zeta potential analysis for Au nanofluids and observed acceptable stability. Zhu et al. [10] studied Alumina-water based nanofluids at various pH levels and at different surfactant concentrations.

3.1.4 L*ight Scattering and Electron Microscopy techniques*

Imagery analysis of the nanofluids can be done by using electron microscope namely Scanning Electron Microscope (SEM) or Transmission Electron Microscope (TEM).Usually TEM is preferred over SEM in case of nanofluids and most of researchers utilize TEM for their characterization. Cryogenic transmission electron microscope has the capability to provide a more powerful and reliable characterization technique but its available in very few laboratories. Sanning Probe Microsopy (SPM) did not find much use for characterization. A very simple method represents particle size analysis on basis of Dynamic Light Scattering (DLS). Most researchers have utilized DLS technique to determine for particle size distribution and then corroborate the results with TEM as main characterization tool. Other important characterization tools for the structure and morphology nanoparticles are the Small Angle X-ray Scattering (SAXS) and Small Angle Neutron Scattering (SANS).

3.2 Methods to Increase Stability

3.2.1 Use of Ultrasonic Agitators

After nanofluids have been prepared, agglomeration may occur over time which can result in even faster sedimentation rates of particles because large clustered particles show the tendency to settle down quickly under the action of gravity alone. Ultrasonic agitation can break those clustered particles back into individual particles and it depends on how long the nanofluid sample was kept in the agitator as demonstrated by Manson et al. [11]. Wang et al. [6] Investigated two different nanofluids; carbon black-water and silver-silicon oil and they utilized high energy of cavitation for breaking clusters among particles and again it was observed that there were less clustered particles in samples that were kept in agitator for longer time durations [12].

3.2.2 Surface modification techniques

This technique does not require a surfactant. It involves the addition of functional particles into the base fluids which are capable of providing very stable nanofluids. There are several of examples of these modification techniques. Yang et al. [13] experimented with addition of silanes to the surface of silica nanoparticles in the solution. It was observed that there was no deposition layer formation on the heating surface after the pool boiling process. Another way to increase stability of carbon nanotubes is by adding hydroxyl groups onto their surface [14]. These techniques, although complex, have shown to increase stability of nanoparticles that otherwise tend to agglomerate. Another test was conducted to synthesize nanofluids containing single as well as double walled CNTs by wet mechanochemical reaction without the use of surfactants. Data from the infrared spectrum & zeta potential tests represented that hydroxyl groups had attached onto CNT surfaces [16].

3.2.3 Surfactant Addition

Surfactants added in nanofluids are also termed as dispersants. It is an easy and economical method to achieve the stability of nanofluids. Surfactants tend to have an effect on surface characteristics even when added in small quantities. They consist of a hydrophobic portion called the TAIL which is generally a long-chain hydrocarbon, and a hydrophilic portion called the HEAD. They are added to increase the surface contact of two materials which is also termed as wet ability. Generally in case of two-phase systems, the surfactant tends to position itself at the interface of the two phases and maintains a degree of continuity to some extent between the particles and the base fluid. Depending upon the type of the head, they are broadly classified into four categories namely a) nonionic (without any charge groups in its head), b) anionic (negatively charged head groups) c) cationic (with positively charged head groups) and d) amphoteric (with zwitterionic head group). Selection of the right type of surfactant is very important. Generally if the base fluid used is polar solvent then its necessary to select water-soluble surfactants otherwise oil soluble ones can be selected. In the case of nonionic surfactants the solubility through hydrophilic/lipophilic balance (HLB) value can be evaluated. A lower HLB value indicates more oil soluble surfactants, whereas a higher HLB number represents a more water-soluble surfactant. Although it is an effective way to increase stability of nanoparticles, it can lead to several problems like contaminating heat transfer media, produce undesirable effects like foaming etc. during heating or cooling, effect thermal properties of the nanoparticles and base fluid like reduced enhancement in thermal conductivity [15].

4. THERMO PHYSICAL PROPERTIES

Experimental studies have shown that the thermal conductivity of nanofluids largely depends on different factors like particle volume fraction, material used, particle size and shape, base fluid used and also the temperature. The amount and types of additives along with the acidity of the nanofluid were also responsible in the enhancement of the thermal conductivity. Dynamic thermal conductivity along with the viscosity are largely dependent on volume concentration of nanoparticle and other parameters like particle shape and its size distribution, mixtures used and slip mechanisms, dispersants, etc. Studies have also showed that thermal conductivity and viscosity both increase by adding nanoparticles in the base fluid as compared to the base fluid itself. So far till date many theoretical and experimental values have provided us with various correlations that have been proposed for thermal conductivity as well as viscosity of these fluids. However, till now no general correlations have been developed because of lack of mutual understanding on their mechanisms.

4.1. Effects on Viscosity

The particles when dispersed in a fluid may come close to each other and form aggregates of sizes greater than the original particle size which, as a result, tend to settle down due to gravity. Stability in nanofluids means that there is very low aggregation of the particles. The aggregation rate is practically determined by the collisions frequency and the probability of particles joining together during collisions. Another research was done to analyze the dispersion and stability characteristics of nanofluids prepared by dispersing CuO nanoparticles. The behavior characteristics based on concentrations by volume at high pressures of 45 MPa and viscosity at atmospheric pressure were investigated experimentally. It was observed that the effect of particle size on density was not substantial but still it could not be ignored. Also the viscosity differences were very large and required to be taken into consideration for practical applications. These viscosity differences could be explained qualitatively with the help of a theory explaining both, the state of aggregation and the distribution of particle size of the nanofluid. Tran X. Phuoc et al [17] have given some experimental observations based on the shear rate effects and particle concentrations by volume on the shear stress and the viscosity behavior of nanofluids prepared by dispersing Fe_2O_3 along with Polyvinylpyrrolidone (PVP) or Polyethylene oxide, (PEO), as a dispersant. The observations made clearly show that these fluids experienced a yield stress and behaved like shear-thinning non-Newtonian fluids. The yield stresses were reduced to Newtonian limit, as the particle volume fraction was reduced but still existed at low particle concentrations by volume.

4.2. Effects on Thermal Conductivity

A large number of experimental and theoretical studies have been conducted in the literature to determine a standard correlation for thermal conductivity of nanofluids. M.M. Elias et al. [18] presented a research paper for the thermo physical properties of Al_2O_3 nanoparticles dispersed into water along with ethylene glycol used as coolant in automobile radiator. The nanofluids were prepared by the two-step method utilizing an ultrasonic homogenizer but without any surfactants. Thermo physical properties like conductivity, viscosity and specific heat were determined at different volume concentrations of nanoparticles at different temperatures. The results showed that thermal conductivity, viscosity, and density of the nanofluid increased when the particle concentration was increased but the specific heat of nanofluid showed a decrease. Moreover, with increase in temperature, thermal conductivity and specific heat were increased but the viscosity and density were decreased.

Madhusree Kole, T.K. Dey [19] investigated the viscosity of the nanofluid synthesized from alumina nanoparticles dispersed in commercial car coolant. The nanofluid mixed with predetermined quantity of oleic acid surfactant was observed to be stable for more than 80 days. The effects of volume fraction and temperature on viscosity were determined. Whereas the pure base fluid exhibited Newtonian behavior at the measured temperature, it changed into a non-Newtonian fluid after the addition of a small quantity of alumina nanoparticles. Their results prove that viscosity of the nanofluid increased with increasing concentrations and decreasing temperatures. Most of the previously predicted models under estimate the values of the measured viscosity. Dependence of the nanofluid viscosity on volume fraction is predicted quite well by most of the given correlations for nanofluids that consider the effect of Brownian motion of nanoparticles. Similar results were given by other researchers also [32].

L. Syam Sundar et al. [20] investigated the experimental and theoretical effect on thermal conductivity and viscosity of magnetic Fe_3O_4 water nanofluid. The nanofluid was synthesized by first preparing Fe_3O_4 nanoparticles utilizing chemical precipitation method, and then a sonicator was employed to disperse them in water. Thermal conductivity & viscosity were observed to increase with increasing particle concentration. Viscosity enhancement was more as compared to thermal conductivity enhancement at any given concentration & temperature. Theoretical correlations were predicted to give the properties of nanofluids without having to revert back to the Maxwell and Einstein correlations, respectively.

4.3. Heat Transfer and Pressure Drop

The effective enhancement of thermal conductivity is very important for the improved heat transferring behavior of the fluids. Various other variables also play important roles in the observed results. For instance, the heat transfer coefficient in the case of forced convection in tubes may be affected by several physical quantities that are related to the fluid as well as geometry of the given process system through which the flow is being tested. These quantities often are the intrinsic properties like thermal conductivity, specific heat, density or viscosity of the fluid as well as the extrinsic system properties like the tube diameter, length, flow velocity etc. A.A. Abbasian Arani et al. [22] investigated the effect of nanoparticle concentration on the convection heat transfer coefficient along with pressure drop of TiO_2 water nanofluids with particle concentration between 0.002 and 0.02 by volume and Reynolds ranging from 8000 to 51,000. The experimental setup used was a horizontal double tube counter-flow type heat exchanger. The results showed that by increasing the Reynolds number or particle concentration, the convective heat transfer capability increased. But it is well known that all nanofluids show higher Nusselt number as compared to the distilled water itself. But for using the nanofluid at higher

Reynolds number, much more pumping power was required to compensate for the pressure drop in nanofluid, whereas the increase in the Nusselt number with respect to all Reynolds numbers is approximately the same. Hence the use of nanofluids at higher Reynolds numbers as compared to lower Reynolds numbers shows very less benefits. Deepak Kumar Agarwal et al. [23] studied the turbulent convective heat transfer characteristics of kerosene- Al_2O_3 nanofluid in a horizontal circular experimental configuration using a closed loop setup. The purpose was to identify the possibilities of use of kerosene-Al_2O_3 nanofluid in the regenerative cooling of the thrust chamber in a semi-cryogenic rocket engine. The particle size variation effects, effects of concentration from 0.05% to 0.5% and effects of Reynolds number on convective heat transfer & pressure drop were explained. Heat transfer performance of the nanofluid is calculated with respect to identical Reynolds number, Peclet number and velocity. Further detailed study of experimental data predicted that in most cases, heat transferring properties were significantly higher as compared to the pure base fluid i.e. kerosene. Higher increase in heat transfer coefficient was noticed for larger sized particles compared to smaller sized ones although the measured thermal conductivity was showed to be higher for smaller sized particle. A correlation to determine the total heat transfer characteristics of nanofluids is also determined, which indicates the advantages of these fluids with respect to their thermo physical properties. The observations also highlight the importance of Prandtl number in convective heat transfer characteristics.

Vahid Delavari, Seyed Hassan Hashemabadi [24] attempted to explain turbulent & laminar flow heat transfer characteristics by simulation of nanofluid flow in flat tube in 3D by using computational fluid dynamics (CFD). The behavior and characteristics of pure water & pure ethylene glycol were compared with the observed results. The heat transfer coefficients from both methods were compared with those of different particles concentrations. A minute change in the friction factors was observed in the system and the convective heat transfer coefficient of the second model was quite different from that of the first model.

1. APPLICATION OF NANOFLUIDS

The concept of nanofluids came into existence about two decades ago. Their potential in heat transfer or cooling applications has continuously attracted increasing attention. Up till now, there were some research papers which presented overviews of different aspects of these nanofluids. Because of higher density chips, the design of more compact electronic components makes heat dissipation even more difficult. All advanced electrical or electronic devices are facing heat management challenges due to the increased levels of heat generation and the reduction in the surface area for heat rejection or dissipation. So a reliable heat management system is very important for the continuous and smooth working of these modern electronic devices. Generally, there are two alternatives for improving the heat dissipation for the electronic equipment. First one is to find the best geometry for cooling devices; second one is to increase their capability to transfer heat. Nanofluids with very high thermal conductivities also have high convective heat transfer coefficients when compared to their base fluids. Recent reviews showed that nanofluids can increase the heat transfer coefficient as well as the thermal conductivity of a fluid or coolant.

Nanofluids have very high potential in improving automotive industry and cooling rates of heavy-duty engine by increasing efficiency, reducing the weight and complexity of heating/cooling systems. The increased cooling rates for automobile and truck engines can also be used to reject more heat energy from higher output engines using the same sized cooling system. Also on the other hand it would be beneficial to design even more compact cooling system with radiators which are smaller and lighter. It would also be beneficial as it would increase the performance and fuel economy and performance of cars and trucks. Nanofluids based on Ethylene glycol have recently attracted attention in the possibility of use as engine coolant [18, 24, 32] because of the low-pressure working conditions compared to a 50/50 mixture of water and ethylene glycol, which is the most commonly used automobile coolant. These nanofluids have a very high boiling point, and these can be used to increase the working temperatures of normal coolants and also remove more heat utilizing the already existing cooling systems.

In Space and Defense sectors, because of the restriction of space, weight, and available energy in space stations and aircrafts, there is a very strong demand for highly efficient heating/cooling systems which are as small in size as possible. The Nanofluids with very high heat fluxes are capable of providing the necessary cooling/heating rates in such applications and in other systems of the military or defense and space sectors, which may include military vehicles and submarines or even high-power laser. Therefore, the applications of nanofluids range widely especially in the fields where density of power is very high and the equipment needs to be smaller and lighter.

Over the last two decades, drug delivery systems based on nanoparticles have also been developed so as to increase the efficiency of the drug action. The very small-sized, customized surface improves the soluble properties and the multi functional aspects of the nanoparticles open many opportunities and create new applications in the field of biomedicines. These properties of nanoparticles offer the capability to interact with the complex cellular functions of the organisms in better ways.

6. CONCLUSIONS

Although these fluids have displayed extremely exciting possible applications, some crucial problems also need to be resolved before commercial use of nanofluids is to be started. The following important points require the attention of the researchers:

- More experimental and theoretical research needs to be done to determine the important factors affecting the performance of these fluids. Up till now, there is some degree of disagreement between results given by different research groups therefore it is necessary to identify the factors contributing to such results.
- The increased in viscosity by the addition of nanoparticles is a crucial drawback because it increases the pumping power requirements. The potential applications of nanofluids with less viscosity and high conductivity are important. Improving the compatibility amongst different nanomaterials and the base fluids by means of modifying the interface properties of two phases may also be one of the possible solutions.
- The shape of dispersants or additives in nanofluids is vital to the properties; hence new nanofluid preparation processes with controlled microscopic structure will be important in research work.

- Stability of colloidal suspensions is an important concern for both research as well as applications. Their stability, especially for long term in the practical conditions after thousands of operational cycles should be given more attention.

Finally, the lack of investigation in the thermal characteristics of these fluids at very high temperatures need to be addressed, which may lead to other possible applications of nanofluids in fields like high-temperature absorption of solar energy, storage etc.

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