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# A REVIEW ON THE INFLUENCE OF NANOPARTICLE SIZE IN THERMAL ENHANCEMENT OF CuO-WATER NANOFLUIDS AND THEIR CHARACTERISTICS

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## Abstract

Nanofluids are made of both a base fluid and a volume fraction of dispersed nanoparticles, with sizes within the range of 1-100nm. Nanofluids demonstrates specific thermo-physical properties and characteristics and some authors deals with nanofluid as being colloids, mainly due to their non-Newtonian behavior, viscoelastic properties, shear stress behavior, etc. The most common nature of nanoparticles are different types of carbons (e.g. diamonds, graphite, carbon nanotubes, etc.), metallic (e.g. Gold, Copper, Silver, Steel, etc.) or even metallic oxides (e.g. CuO, SiO, $Al_2O_3$, ZnO, etc.). There is still a challenge to accurately compare the available nanofluid results usually due to the fact that some nanofluid types have just a few data available, which would demand additional experimental data for proper correlations and comparisons among them. From all nanofluid types currently available in the literature it is clear that both $Al_2O_3$ (alumina) and CuO (copper oxide) are the most common nanoparticles and water is the most common base fluid. Taking into account the material compatibility for several applications, the $Al_2O_3$–water nanofluid has become a very interesting and widely studied nanofluid followed by CuO-water nanofluid, which will be focus of the present work. There are also several CuO-water nanofluid publications with some different nanoparticle sizes available for research and it is reasonable that nanoparticle size represents one of the aspects to be taken into consideration when the analysis of thermal enhancements are in focus. Therefore, this study aims to evaluate some available results in literature for CuO-water nanofluids, by comparing the obtained thermal enhancement results with the nanoparticle sizes used in each respective study, in order to provide some statistical trend lines through the reviewed data by using a CuO-water nanofluid based on their particular characteristics.

## Introduction

The study of nanofluids has been increasing during the last years since Choi (1995) established the term "nanofluids". Several nanofluid thermo-physical properties and their characteristics have been experimentally tested and also studied such as viscosity, density and thermal conductivity. Thermal conductivity is the most widely studied nanofluid property due to the fact that it is related to the increase on the nanofluid thermal enhancement levels obtained when compared to the base fluids alone. Nanofluids demonstrate specific thermo-physical properties and characteristics in such a way that some authors deals with nanofluid as being colloids, mainly due to their non-Newtonian behavior, viscoelastic properties, shear stress behavior, etc. Related to the base fluids used for nanofluid preparations the most commons found in literature are: water, ethylene glycol and engine oil. There are a reasonable number of publications released in the last decade, which increased particularly in the last years. They put together both the base fluids and nanoparticles afore mentioned generating some nanofluids types which were tested, from aerospace to electronics applications, and extending to automotive as well.

According to Das et al. (2008) nanofluids are made of a base fluid with dispersed nanoparticles in the range size of 1 to 100nm, so the statement of nanoparticle size range differs nanofluids from other fluid types. The study of nanoparticle size and its influence on thermal conductivity has been of great interest for several authors (Das et al., 2008). Some theoretical and experimental studies included the impact of nanoparticles sizes in their models. It is common to find out in literature the estimative of average nanoparticle sizes through statistical data over arrange of nanoparticle size distribution. It is unusual to obtain the exact same nanoparticle size over a whole volume concentration (vol. %) of nanoparticles used in any nanofluid. In the preparation process of a nanofluid, the nanoparticle sizes can vary according to some other parameters as for example, volume concentration and time of sonication. So the thermal enhancement related to nanoparticle size is affected by these parameters as well (Bhupender et al., 2014).

Pastoriza-Gallego et al. (2010) experimentally studied the influence of CuO nanoparticle sizes in other parameters as density and viscosity whose are both related to thermal enhancement of CuO-water nanofluids. Nguyen et al. (2007) studied the influence of CuO nanoparticle size and temperature in CuO-water nanofluid viscosity levels. Corcione (2011) prepared a correlating equation for thermal conductivity based on several available data in literature, including CuO-water nanofluids. The outcomes demonstrated that as nanoparticle size increases thermal enhancement ratio decreases and vice-versa. Wang et al. (2009) demonstrated that surfactants applied to CuO-water nanofluids, tends to decrease the nanoparticle size distribution due to better nanofluid stabilization and elimination of nanoparticle agglomerations.

Specifically on the CuO-water nanofluid, there is a difference between water and CuO thermal conductivity. For instance, the distilled water (DI-water) thermal conductivity is around 0,59W/m.K at room temperature while the available publications at the same temperature, in general, have reported the CuO-water nanofluid thermal conductivity values between 10-50% higher than DI-water. It has been noticed that nanofluids always provide much higher heat transport capacity than the base fluid alone. The dispersion among the several thermal enhancement values found in the literature are in a general manner mainly due to some aspects, which also generated some theories (e.g. nanolayer formation, collision between base fluid molecules, Brownian movement interference at low volume fraction levels, thermal induction fluctuation, etc.).

Some of the aspects that were identified as direct contributors for thermal enhancement results dispersion found in the literature can be summarized as follows:

1) Nanoparticle volume fraction (vol. %) or mass fraction (wt. %);
2) Nanoparticle shape and geometry;
3) Operating temperature, as some studies have demonstrated that the temperature causes positive influence for higher thermal enhancements;
4) Nanofluid preparation method, which usually is one-step or 2-steps, as it influences parameters related to stability, sedimentation levels, dispersibility, chemical compatibility of nanoparticles, thermal stability and addition of surfactants;
5) Type of application, as it may change the nanofluid working conditions, for instance, in terms of bubbles formation, viscosity level, clogging formation, etc.;
6) Nanoparticle sizes, which will be focus of this review.

Regarding the nanoparticle size, some authors have reported that it has been a challenge to accurately obtain this characteristic evenly distributed in a given volume fraction (vol.%), which is mainly because of nanoparticle manufacturing process and tolerances. It means that, when a sample of spherical nanoparticles is said to be 30nm for example, this means an average diameter of all the amount of nanoparticles included in the volume fraction (sample size or weight). Thus, it means that throughout the sample size it is possible to find out different diameters than 30nm or even diameters which are close to 30nm or surrounding the 30nm value with great dispersion. Therefore, some authors concerned to this issue, decided to make a weighted evaluation by using a statistical model (e.g. Gaussian distribution) in order ponder the nanoparticle size as close as possible to the real value, in such a way that they cold have more accurate interpretations on their result analyses.

Considering the dispersion on information regarding the thermal enhancement obtained when using nanofluids, this study aims to evaluate some available results for CuO-water nanofluids, by comparing the obtained thermal enhancement results with the nanoparticle sizes used in each respective study. The main objective is to provide some statistical trend lines through the reviewed data by using a CuO-water nanofluid based on their particular characteristics.

**Nanoparticle Size Characterization Processes**

The nanoparticle size is usually determined through a statistical distribution over a range of sizes. The characterization process involves some of the analysis methods as described below:

a) Dynamic Light Scattering (DLS), where a certain intensity of light scattered by a single nanoparticle relates to the nanoparticle volume (Ghadimi et al., 2011);

b) Typical XRD (X-Ray Diffraction) patterns, where the intensity and broadness of XRD peaks suggests the size of nanoparticles. Through photon beam energy, it is possible to know the amount of radiation absorption by a given material when controlled X-ray intensity, is transmitted to it (Künzel and Okuno, 2012);
c) SEM (Scanning Electrons Microscope) and TEM (Transmission Electron Microscope), which are both very helpful for determining the nanoparticle size and distribution through imaging of the nanoparticles, also demands a stable nanofluid for a proper evaluation (Ghadimi et al., 2011).

After the characterization process it is possible to estimate over a volume concentration (vol. %) the percentage of average nanoparticles at a certain size (nm). It is also relevant to mention there is a relation between the nanoparticle size and shape and volume concentration as demonstrated by Bhupender et al. (2014) where different sizes and shapes (e.g. nanorods, nanowires, and nanospheres) of CuO nanoparticles was compared among them, in terms of thermal conductivity levels.

Figure 1 give an example of 0,005% vol. of CuO nanoparticle size distribution in water from experimental data performed by Pastoriza-Gallego et al. (2010). In this case it was adopted the average nanoparticle diameter of 11nm ±3nm for calculations and data comparisons. It is possible to identify the normal distribution of the Gaussian curve for the measured nano-diameters versus the frequency of appearance in arbitrary unit. Indeed, from Fig. 1, it is possible to identify a small amount of nanoparticle sizes, which are out of the used range of 11±3nm as most of the nanoparticle sizes are within the range. In terms of percentage, around 76% of the measured CuO nanoparticles are within the size range of 11 nm ±3 nm, while 10% are in the range of 15 nm ±1nm, also 9,5% are within the range of 6 nm ±2nm and only 4% of CuO nanoparticle sizes are in the range of 18 nm ±2nm.

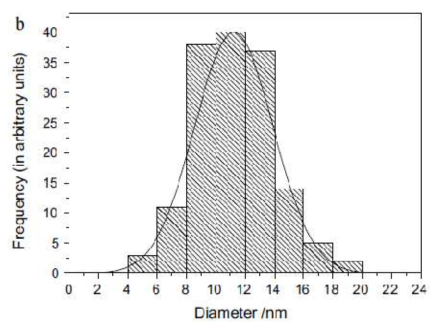


**Figure 1 – Size distribution of 0,005%vol. of CuO nanoparticles in water from Pastoriza et al. (2010).**

The CuO nanoparticle sizes was obtained through a nanopowder synthesis procedure. Some of the factors that work together to modify the thermo-physical properties of CuO nanofluids are: nanoparticle size, shape and volume fraction (Pastoriza et al., 2010). In some comparative analysis, some authors have identified that commercial nanoparticles from some suppliers, usually have a size distribution much more disperse than synthesized ones (Pastoriza et al., 2010; Lee et al., 2014). The method of distribution size for determination of nanoparticle sizes over a volume fraction dispersed in a nanofluid, is commonly found in available literature (Pastoriza et al., 2010; Lee et al., 2014; Shi and Chopra, 2010).

**Thermal conductivity models related to nanoparticle sizes**

From the available literature review, it is possible to mention some of the thermal conductivity models applicable for CuO-water nanofluids. Table 1 gives a summary of these models and demonstrates how each model consider nanoparticle size influence on the thermal conductivity or thermal enhancement ratio.

**Results and comments**

Table 2 summarizes some results from the literature review, which somehow correlated nanoparticle size with thermal enhancement. The thermal conductivity determination depends on other parameters besides nanoparticle sizes, thus in a trial to compare them, it was also included volume fraction, temperature and sonication time.

**Table 1 – A summary of some thermal conductivity models related to nanoparticle size.**

| Author [Ref.] | Model | Comments |
|---|---|---|
| Maxwell, 1881 [11] | $\frac{k_{eff}}{k_f} = \frac{k_p + 2k_f + 2\emptyset_p(k_p - k_f)}{k_p + 2k_f - \emptyset_p(k_p - k_f)}$ | Based on spherical particles, random suspensions which must be under conduction solution theory through stationary conditions. |
| Hamilton-Crosser, 1962 [12] | $\frac{k_{eff}}{k_f} = \frac{k_p + (n-1)k_f + (n-1)\emptyset_p(k_p - k_f)}{k_p + (n-1)k_f - \emptyset_p(k_p - k_f)}$ | For high concentrantions of spherical particles under conditions of differential effective medium (DEM) theory. |
| Prasher et al., 2005 [13] | $k_{eff} = (1 + ARe^m Pr^{0,333}\emptyset_p)\left[\frac{k_p + 2k_f + 2\emptyset_p(k_p - k_f)}{k_p + 2k_f - \emptyset_p(k_p - k_f)}\right]k_f$ | Obtained from Maxwell model and included the effects of convection generated by the Brownian motion |
| Koo and Kleinstreuer, 2005 [14] | $k_{eff} = k_{static} + k_{Brownian}$<br>$k_{static} = \frac{k_p + 2k_f + 2\emptyset_p(k_p - k_f)}{k_p + 2k_f - \emptyset_p(k_p - k_f)}$<br>$k_{Brownian} = 5\,x\,10^4 \beta\emptyset_p\rho_p C_p \sqrt{\frac{k_B T}{\rho_p D}}(T, \emptyset_p)$ | Considers the effects of surrounding liquid motion with random nanoparticles movement. Based on static Maxwell theory and dynamic effect of Brownian motion |
| Yu-Choi, 2003 [15] | $k_{eff} = \frac{k_p + 2k_f + 2\emptyset(k_{pe} - k_f)(1+\beta)^3}{k_{pe} + 2k_f - \emptyset(k_{pe} - k_f)(1+\beta)^3}k_f$<br>$k_{pe} = \frac{2(1-\gamma) + (1+\beta)^3(1+2\gamma)\gamma}{-(1-\gamma) + (1+\beta)^3 + (1+2\gamma)}k_p$<br>$\gamma = k_{lr}/k_p$ | It was based on Maxwell model but additionally taking in account the effects of nanolayer thickness and thermal conductivity (TC) parameters |
| Corcione, 2011 [5] | $\frac{k_{eff}}{k_f} = 1 + 4.4Re^{0.4}Pr^{0.66}\left(\frac{T}{T_{fr}}\right)^{10}\left(\frac{k_p}{k_f}\right)^{0.03}\emptyset^{0.66}$ | Correlation based on a wide variety of experimental data from literature in the ranges of nanoparticle sizes, temperature and volume fractio of 10-150nm, 294-324K and 0,002-0,09 respectively. Nanofluid types aplicable for this model are: $Al_2O_3$, $TiO_2$, Cu and Cuo dispersed in both $H_20$ and EG. |

**Table 2 – Different nanoparticle sizes applied in CuO-water nanofluid and their respective thermal enhancement ratios.**

| Author [Ref] | CuO Nanoparticle Size (nm) | Thermal Enhancement ratio | Volume fraction (vol. %) | Temperature (°C) | Sonication time (h) |
|---|---|---|---|---|---|
| Karthikeyan et. al [16] | 8 | 1,02 | 0,02 | 20 | 0,5 |
| | 8 | 1,08 | 0,09 | 20 | 0,5 |
| | 8 | 1,13 | 0,1 | 20 | 0,5 |
| | 8 | 1,19 | 0,3 | 20 | 0,5 |
| | 8 | 1,25 | 0,8 | 20 | 0,5 |
| | 8 | 1,316 | 1 | 20 | 0,5 |
| Nemade et. al [17] | 33 | 1,197 | 0,5 | 55 | 1 |
| | 42 | 1,134 | 0,5 | 55 | 0,75 |
| | 46 | 1,124 | 0,5 | 55 | 0,5 |
| | 53,5 | 1,087 | 0,5 | 55 | 0,25 |
| Khedkar et al. [18] | 25 | 1,05 | 0,01 | 26 | 1,5 |
| | 25 | 1,12 | 0,02 | 26 | 1,5 |
| | 25 | 1,13 | 0,03 | 26 | 1,5 |
| | 25 | 1,16 | 0,04 | 26 | 1,5 |
| | 25 | 1,17 | 0,05 | 26 | 1,5 |
| | 25 | 1,32 | 0,075 | 26 | 1,5 |
| Wang et al. [19] | 42,5 | 1,08 | 0,02 | 25 | not informed |
| | 42,5 | 1,1 | 0,04 | 25 | |
| | 42,5 | 1,11 | 0,1 | 25 | |
| | 42,5 | 1,125 | 0,15 | 25 | |
| | 42,5 | 1,16 | 0,4 | 25 | |
| Priya et al. [20] | 50 | 1,02 | 0,004 | 28 | 6 |
| | 50 | 1,06 | 0,008 | 28 | 6 |
| | 50 | 1,1 | 0,012 | 28 | 6 |
| | 50 | 1,13 | 0,016 | 28 | 6 |
| | 50 | 1,05 | 0,004 | 50 | 6 |
| | 50 | 1,16 | 0,008 | 50 | 6 |
| | 50 | 1,25 | 0,012 | 50 | 6 |
| | 50 | 1,32 | 0,016 | 50 | 6 |
| | 50 | 0,95 | 0,004 | 55 | 6 |
| | 50 | 1,24 | 0,008 | 55 | 6 |
| | 50 | 1,33 | 0,012 | 55 | 6 |
| | 50 | 1,43 | 0,016 | 55 | 6 |

(*) average nanoparticle size

As demonstrated in Table 2, there is a considerable variation among the values and most of the authors considered a fixed nanoparticle size varying the temperature, sonication time and volume fraction. For example, when Khedkar et al. (2012) and Wang et al. (2009) are compared to each other, it is possible to find similar thermal enhancement ratios up to volume fractions up 0,1% vol. Above 1% vol, Khedkar et al. (2012) demonstrated higher thermal enhancement ratios. Even though Wang et al. (2009) used nanoparticle sizes of average of 42.5nm, against 25nm average size from Khedkar et al. (2012), the thermal enhancement ratios above 1% vol. for Khedkar et al. (2012) were higher than Wang et al. (2009). This behavior repeated for other comparisons. Thus, it brings an understanding that nanoparticle size effect is more critical for smaller vol.% than higher vol.%. Another understanding is that nanoparticle sizes can vary with different sonication time, surfactant use and nanoparticle agglomeration as time passes as well. In some applications as pulsating heat pipes (PHP), nanoparticle agglomeration may be useful to control the bubble formation and nucleation sites (Riehl and Santos, 2012).

Figure 1 compare the nanoparticle impact on thermal enhancement ratio for some authors. With a fixed nanoparticle size and variations on other parameters (e.g. sonication time, volume fraction, etc.), it is possible to obtain similar thermal enhancement ratios between two nanofluids with different nanoparticle sizes. However, Nemade et al. (2016) results demonstrated an estimative on the effect of nanoparticle size in the thermal enhancement ratio. By fixing other parameters (e.g. sonication time, volume fraction), it is possible to verify that thermal enhancement decreases as nanoparticle size increases through linear regression approximation with $R^2$ =0.9769.

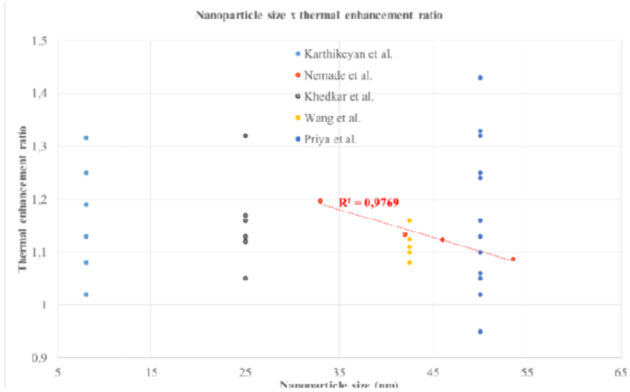


**Figure 1 – Nanoparticle size impact on thermal enhancement ratio for some authors.**

Figure 2 demonstrates the results obtained by Priya et al. (2012), which considered fixed sonication time, temperature and nanoparticle size. It is possible to verify the variation of thermal enhancement ratio in function of the volume fraction in a range between 0,004 and 0,016 vol.%. As volume fraction increases thermal enhancement ratio also increases for a fixed nanoparticle size. However, as demonstrated in Fig. 1 and Table 2, the impact of nanoparticle size on thermal enhancement ratio is more effective at higher volume fractions. The nanoparticle size effects observed at small volume concentrations became less evident for higher vol.%, consequently as nanoparticle increases the thermal enhancement ratio decreases.

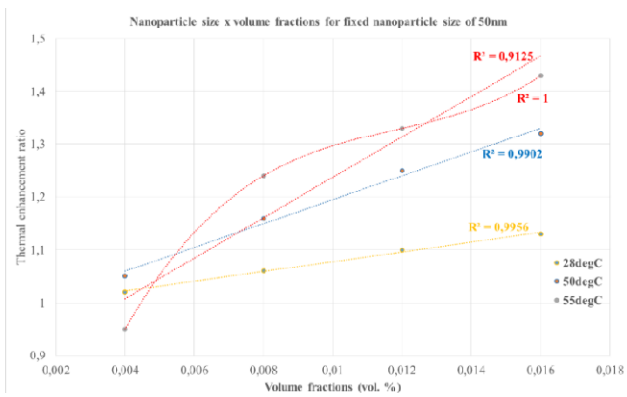


**Figure 2 – Fixed nanoparticle size and variable volume fraction thermal enhancement Impact.**

## Conclusions

The following conclusions can be derived from this study, as follows:

- Nanoparticle size can vary according to sonication time;
- As nanoparticle sizes increases, the thermal conductivity decreases;
- Further investigation is necessary for better understanding on impacts over each size percentage of the statistical nanoparticle size distribution versus thermal enhancement ratio;
- Nanoparticle size can vary according to surfactants application for nanofluid stabilization;
- Nanoparticle size can increase as time passes if clustering and agglomeration are generated due to poor nanofluid stabilization.

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