

Improvement of thermal properties of water and ethylene glycol by metallic and ceramic dispersion

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Abstract. Owing to rising need for more energy efficient coolant systems, the current work focuses on synthesis of Alumina-water, Alumina-Ethylene Glycol (EG), Zirconium-water, Zirconium-Ethylene Glycol particle dispersion systems for use as quenchants, with varying volume of particles obtained using a top-down approach of 10h ball milling. Characterisation of the particles was performed using XRD analysis, also measuring the crystallite size. Particle size measurement was also undertaken by using particle size analyzer, further corroborated by SEM analysis. A zeta-potential study was carried out to obtain the iso electric point for maintaining stability. Synthesis of the dispersions at different volume % of powders were followed by thermal conductivity measurements with water and EG base fluids, with and without addition of oleic acid as a surfactant. The stability studies were performed by visual observation. From the results it was observed that Al_2O_3 and Zr can increase conductivity of EG more prominently than water and stability of Zr based suspensions are better than Al_2O_3 . Oleic acid did not play any positive role in these systems.

Keywords: Dispersion; Thermal conductivity; Water; Ethylene glycol; Surfactant

1. Introduction

The manifold growth in electronics, communication and computing technologies through miniaturization and enhanced rate of operation and storage of data result in enormous amounts of heat, thus demanding cooling capabilities with better performance. Fluids are often used as heat carriers in heat transfer equipment. Instances of significant usage of heat transfer fluids (conventionally water, ethylene glycol and engine oil) are in automotive, aeronautical cooling systems and manufacturing process heating and cooling systems. For use as coolant, thermal conductivity of the fluid plays a vital role in the heat transfer apparatus. The addition of metallic and metallic-oxide particles to coolants used in thermal control systems can intensely increase the thermal conductivity of the solvent.

In dispersion, movement of particles is random, thus carrying comparatively large volumes of enveloping liquid with them. This micro-scale interfacing [1] may occur between areas with a temperature gradient, subsequently resulting in a lowering of local temperature gradient for a given heat flux compared with the pure liquid case. Thus, as a consequence of Brownian motion, the thermal conductivity increases [2]. As heat transfer is prominent at the surface of the particle, greater surface



area is desirable. Given that the stability criterion is fulfilled, microparticles offer high surface areas and reduced viscosity, as opposed to macroparticles. Further, microparticles do not pose a threat of erosion of the channels, unlike macroparticles. The surface to volume proportion is high implying that a very small volume fraction of dispersed particles (very low particle loading) can have a very high surface area (believed to significantly improve the heat transfer characteristics and stability of dispersions) [3]. In the same line, nano sized particle dispersed “nano fluid” has gathered attention in recent years. Many researchers have shown manifold improvement of thermal properties of water and Ethylene Glycol based nano fluids [3-6].

The current work focuses on fabrication of Alumina-water, Alumina-Ethylene Glycol (EG), Zirconium-water, Zirconium-Ethylene Glycol particle dispersion systems for use as quenchants, with varying % by volume of particles obtained using top-down approach. Alumina is a cheap and readily available ceramic oxide and exhibits inherent inertness. A dispersion of alumina in water does not lead to any unwanted chemical interaction owing to its inertness. Pure Zr develops a layer of ZrO on it resulting in its inertness in aqueous media. Addition of common surfactants such as oleic acid was also experimented to influence stability [7].

2. Materials and Methods

2.1. Powder synthesis and characterization

To reduce the size of Al_2O_3 and Zr powders, they were taken in two separate vials of Fritsch Pulverisette planetary ball mill (dual vial system) along with the grinding media i.e. the chrome steel balls. The vials and balls were cleaned with acetone and dried before using them. The ball to powder weight ratio was maintained 10:1. The powders were then milled in a planetary at 300 rpm for 10 hours. The milling was carried out in a wet medium using toluene.

The milled and unmilled powders were characterised by X-ray diffraction (XRD) to identify the phase and to determine the crystallite size. XRD was carried out by Rigaku Ultima-IV X-ray diffractometer using $\text{Cu } K_\alpha$ ($\lambda = 0.15406 \text{ nm}$) radiation. Crystallite size of both the milled powder was calculated from the Scherrer equation as given below:

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

Where, D is crystallite size, λ is X-ray wavelength, β is line broadening at half the maximum intensity and θ is Bragg's angle.

The particle size and zeta potential of the Al_2O_3 and Zr particles were measured using Malvern Nano ZS model particle size analyzer. For that, very small amount of the milled powders were dispersed in distilled water and later pH was changed systematically to find the zeta potential at different pH values and thus to calculate the Iso Electric Point (IEP). The size distribution and microstructure of the milled and unmilled powders was studied by scanning electron microscopy (SEM-JEOL-JSM-6480LV).

2.2. Synthesis of dispersion and characterization

Following the synthesis and characterization of the powders dispersion of the powders were made with distilled water and ethylene glycol with varying degree of dispersion (0.05 vol%, 0.1 vol%, 0.4 vol%, 0.8 vol%). Powders were added in 20 ml test tubes filled with water/ethylene glycol and test tubes were sonicated for 30 minutes. One drop of oleic acid was added as surfactant to prepare stable dispersion by increasing the magnitude of the zeta potential [7], and then they were sonicated again.

The thermal conductivity of the prepared dispersions of Al_2O_3 and Zr was measured using thermal conductivity probe (KD2 pro). The experimental value of thermal conductivity of the dispersions was compared with the theoretical thermal conductivity as calculated using the rule of mixture and Maxwell's effective medium theory [8].

The stability of the prepared dispersions of Al_2O_3 and Zr in water and ethyl glycol was studied over 24 hours of time. The dispersions were kept stationary for 24 hours after which the settling condition of the particles was checked. After the addition of oleic acid the stability of the dispersions were again observed and recorded.

3. Result and discussion

3.1. Particle size analysis and zeta potential measurements by particle size analyser

Fig. 1 (a) shows the particle size distribution of Al_2O_3 particles after milling. The particle size of Al_2O_3 was found to be in range of 700nm to 1700nm. The peak is observed at 1281nm. After milling the Zr, it shows bimodal particle size distribution as evident from Fig. 1(b). Two peaks were observed at 712nm and 5560nm. The particle size lies in the range of 400-1500nm and 4800-6500nm.

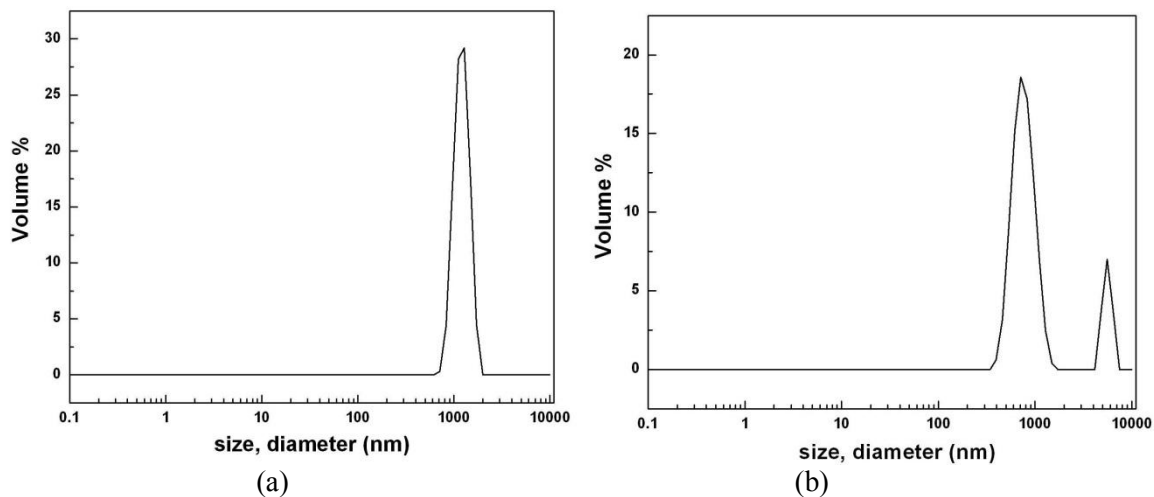


Fig. 1:- Particle size distribution (in terms of diameter) of (a) Al_2O_3 and (b) Zr by volume percentage

Table 1 shows the zeta potential of both the powders at different pH values and from extrapolation of the data the IEP of Al_2O_3 was found to be at $pH \sim 4$ and for Zr $pH \sim 8$. During synthesis of the dispersed fluids the pH values were checked so that the values were away from the IEP, which increases the stability of the suspension by repulsion between each other and reduces the chance of agglomeration.

Table 1: pH vs. Zeta potential of Al_2O_3 and Zr

Al_2O_3		Zr	
pH	Zeta potential (mV)	pH	Zeta potential (mV)
3.1	10.00	5.1	-9.00
3.5	6.73	6.6	-4.39
4.4	-6.53	8.1	-1.44
6.5	-12.00		
9.2	-21.70		

3.2. Characterization by XRD

Fig. 2 shows the XRD plot of unmilled and milled Al_2O_3 and Zr powder. The XRD plot of the milled Al_2O_3 shows significant reduction in intensity of the peaks and a subsequent broadening of the peaks.

The decrease in the intensity of the peaks and the broadening of the peaks after milling can be attributed to the reduction in grain size of Al_2O_3 and, incorporation of lattice strain due to ball milling. The average crystallite size of milled Al_2O_3 as calculated from Scherrer formulae was in the range of 9nm - 38nm. In case of XRD plot of Zr also, the intensity and number of peaks were found to be reduced. Considerable broadening of the peaks was also observed. The crystallite size of milled Zr as calculated from Scherrer formula was in the range of 8nm - 35nm.

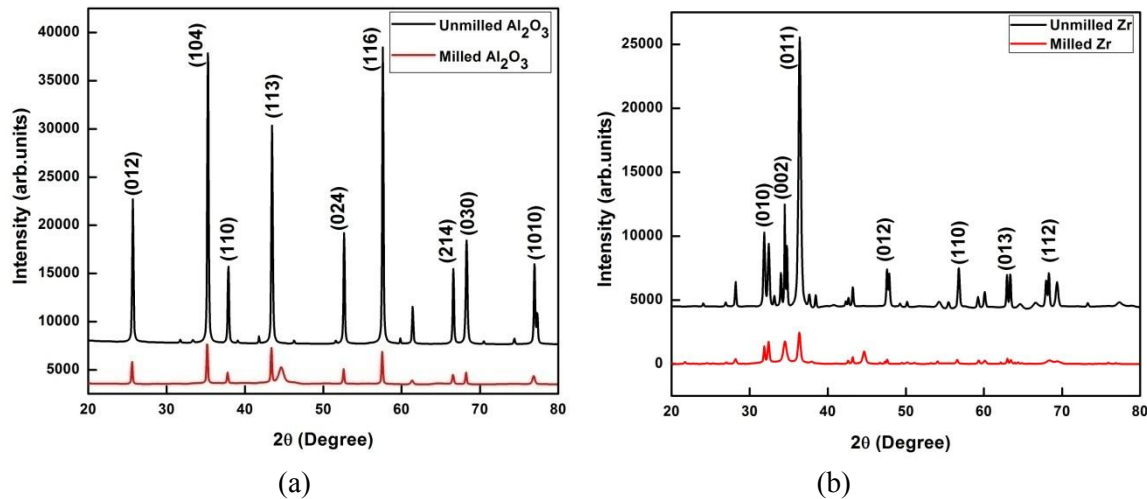


Fig. 2:- XRD profiles of milled and unmilled (a) Al_2O_3 and (b) Zr powders

3.3. Scanning electron microscopy

Fig. 3 shows SEM images of milled powders and from that it is evident that milled powders have homogeneous size distribution. From Fig. 3(a) it seems that the average particle size of milled alumina powder was approximately $2\mu\text{m}$ and the same for Zr powder was found to be finer ($\sim 1\mu\text{m}$) (Fig. 3(b)). The difference in particle size obtained from SEM analysis and particle size analyser can be attributed towards agglomeration of the powder during test.

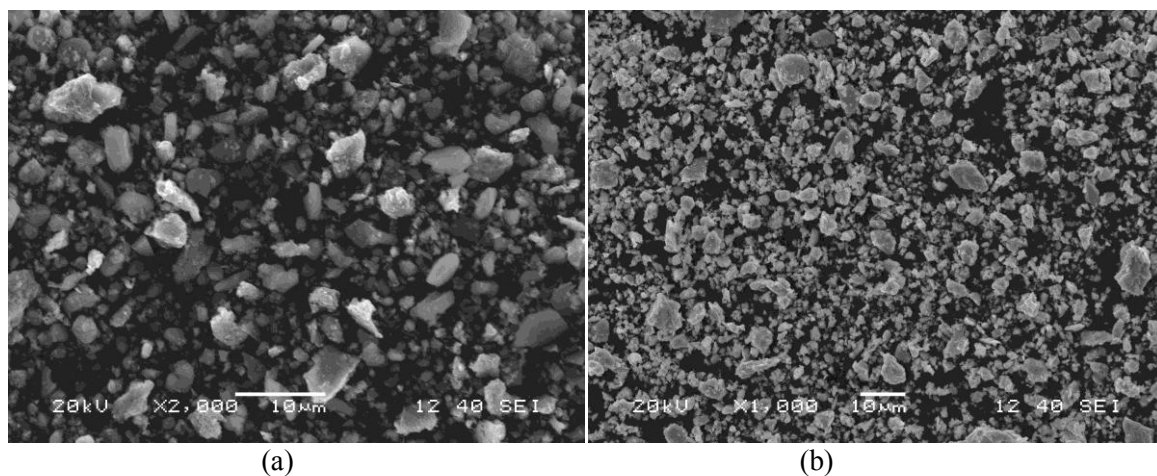


Fig. 3:- SEM images of milled (a) alumina and (b) Zirconium powders

3.4. Thermal conductivity

Thermal conductivity of the dispersions is plotted against volume fraction of the particles. Such plots are displayed in Fig. 4 and 5. The horizontal dotted lines in the plots at $k=1.4\text{W/mK}$ and $k=0.3\text{W/mK}$ represent the measured conductivities of distilled water and pure EG respectively, taken as references. In the figures theoretical plot represents data based on rule of mixture. Plots also include theoretical values calculated based on Maxwell's equation. In both the figures the theoretical conductivities were found to increase with volume % of the particles.

From Fig. 4(a) it can be observed that with increasing alumina amount the conductivity decreases, which may attributed to the agglomeration factor. In case of surfactant addition also similar problem was observed. But, the observed conductivity of 0.05% and 0.1% dispersions are higher than that of water. Thus, minor addition of alumina particle can be helpful to increase conductivity of water. When alumina was dispersed in EG, it was observed that conductivity of all dispersions were higher than that of EG (Fig. 4(b)). But effect of surfactant was not positive as that was observed in water. But conductivity trend was increasing in nature with increase in alumina vol. %. Due to higher density of EG over water it can effectively suspend more particles and thus the suspension shows higher conductivity. Moreover, in EG, chance of agglomeration may be less than water. The theoretical values are completely based on the idea that particles should be there in suspension only and due to this fact the theoretical values are higher than the observed values reported here.

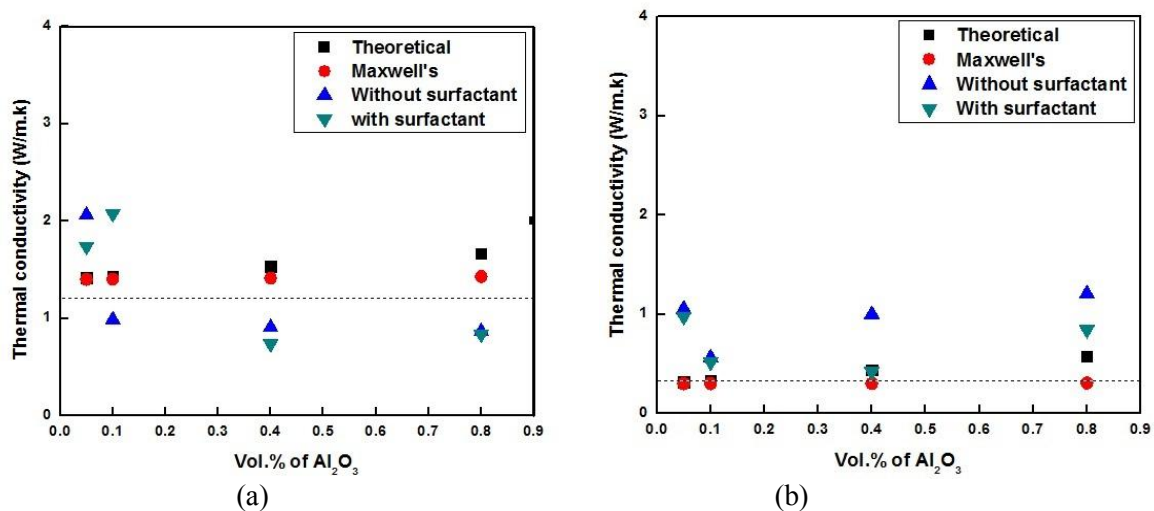


Fig. 4:- Thermal conductivity vs. vol. % of Alumina plot after dispersion in (a) water and (b) EG.

Fig. 5 shows the thermal conductivity nature of Zr based fluids. From Fig 5(a), it was observed that conductivity in water media without surfactant decrease with increasing vol. % of Zr particles possibly due to agglomeration. The trend is similar as was observed in alumina dispersion. However, the observed conductivity with added surfactant shows no such fixed trend. The observed conductivity of 0.05% dispersion alone is higher than that of water.

As shown in Fig 5(b), the observed conductivity of EG based fluid without surfactant rapidly increases from 0.05% to 0.1%. After that, it decreases with further increase in vol. % of Zr particles. The observed conductivity with added surfactant shows no such fixed trend. The observed conductivity of all dispersions is higher than that of EG.

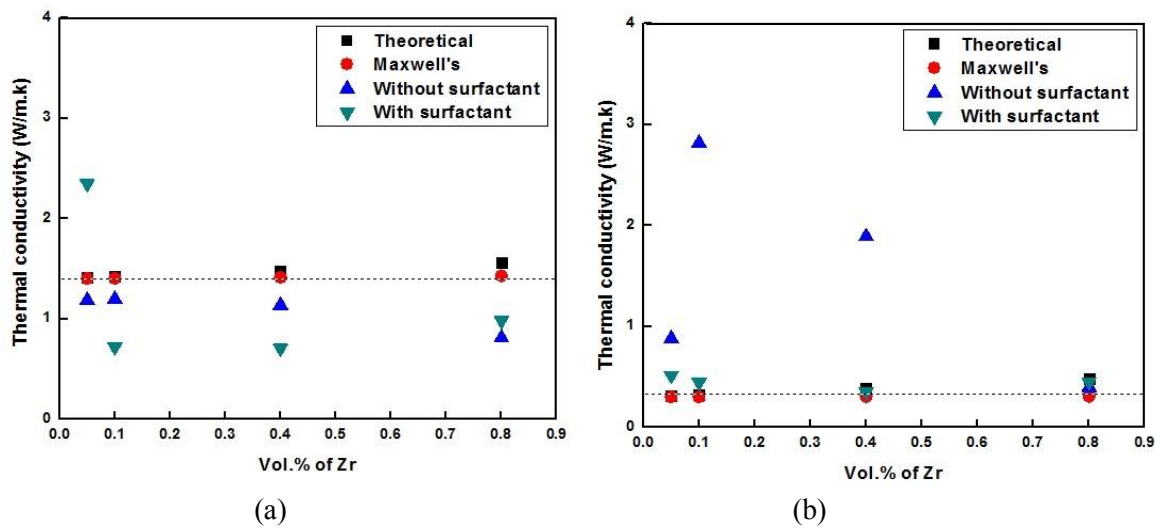


Fig. 5:- Thermal conductivity vs. vol. % of Zr plot after dispersion in (a) water and (b) EG

3.5. Stability study

The stability of the dispersed fluids was checked after 24 hours and the results are summarized in Table 2. From the table it can be observed that only zirconium based fluids having dispersion content up to 0.4% were stable even after 24 hours. This may be attributed towards smaller particle size of Zr compared to Al_2O_3 . Moreover, higher addition of Zr makes it unstable.

From stability study and earlier section it can be observed that oleic acid has negligible effect, mainly in water based dispersion. The solubility of oleic acid is more in EG than in water. For better stability, water soluble surfactants can be tried out [9]. Moreover, though oleic acid can be helpful for better dispersion distribution, its conductivity may also play a negative role in heat transfer as it forms a coating around the dispersed particles [10].

Table 2: Observed stability of the dispersions after 24

Sample	Without oleic acid	With oleic acid
0.05% Al_2O_3 + Water	Unstable	Unstable
0.1% Al_2O_3 + Water	Unstable	Unstable
0.4% Al_2O_3 + Water	Unstable	Unstable
0.8% Al_2O_3 + Water	Unstable	Unstable
0.05% Al_2O_3 + EG	Unstable	Stable
0.1% Al_2O_3 + EG	Unstable	Unstable
0.4% Al_2O_3 + EG	Unstable	Unstable
0.8% Al_2O_3 + EG	Unstable	Unstable
0.05% Zr + Water	Stable	Stable
0.1% Zr + Water	Stable	Stable
0.4% Zr + Water	Stable	Stable
0.8% Zr + Water	Unstable	Unstable
0.05% Zr + EG	Stable	Stable
0.1% Zr + EG	Stable	Stable
0.4% Zr + EG	Stable	Stable
0.8% Zr + EG	Unstable	Unstable

4. Conclusion

From the present study following conclusions may be drawn:

- (i) Al_2O_3 and Zr powders were ball milled and milled powder shows reduction in particle and crystallite size.
- (ii) Thermal conductivity of water was enhanced only by small addition of Al_2O_3 and Zr (0.05-0.1%).
- (iii) Thermal conductivity of EG was enhanced with addition of any amount of Al_2O_3 and Zr.
- (iv) Thermal conductivity improvement was better in EG than water in both Al_2O_3 and Zr.
- (v) Stability of the suspension after 24 hour was found to be better in case of Zr due to its finer particle size.
- (vi) Oleic acid did not show any remarkable positive effects on these systems.

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