THERMAL CONDUCTIVITY IMPROVEMENT IN CARBON NANOPARTICLE DOPED PAO-OIl: AN EXPERIMENTAL AND THEORETICAL STUDY

Shadab Shaikh, University of Dayton, Dayton, OH, 45459, USA
Khalid Lafdi, University of Dayton, Dayton, OH, 45459, USA

Abstract

The present work involves a study on the thermal conductivity of nanoparticle-oil suspensions for three types of nanoparticles namely carbon nanotubes (CNTs), exfoliated graphite (EXG), and heat treated nanofibers (HTT) with PAO-oil as base fluid. To accomplish the above task, first an experimental analysis is performed using a modern light flash technique (LFA 447) for measuring the thermal conductivity of the three types of nanofluids, for different loading of nanoparticles. The experimental results show a similar trend as observed in literature for nanofluids with a maximum enhancement of approximately 161% obtained for the CNT-PAO oil suspension. The overall percent enhancements for different volume fraction of nanoparticles are highest for the CNT based nanofluid followed by the EXG and the HTCNF. The second part of the study includes the formulation of a theoretical model for the effective thermal conductivity of nanofluids. The model is based on a novel point of view regarding the arrangement of nanoparticles in the base fluid. The predictions from the model show a reasonably good agreement with the experimental results. The findings from this study for the three different can have a great potential in the field of thermal management.

Introduction

Low thermal conductivity is a primary limitation in the development of energy efficient heat transfer fluids required in many industrial and commercial applications. The heat rejection requirements are continually increasing due to trends toward faster speeds (in the multi-GHz range) and smaller features (to <100 nm) for microelectronic devices, more power output for engines, and brighter beams for optical devices. Cooling becomes one of the top technical challenges facing high-tech industries such as microelectronics, transportation, manufacturing, and metrology. Conventional method to increase heat flux rates include: extended surfaces such as fins and micro-channels or /and increasing flow rates by increasing pumping power.

However, current design solutions already push available technology to its limits. Conventional heat transfer fluids have inherently poor thermal conductivity compared to solids. Conventional fluids that contain mm- or μm-sized particles do not work with the emerging miniaturized technologies because they can clog the tiny channels of these devices.

New technologies and new advanced fluids with potential to improve flow & thermal characteristics are of critical importance. Inclusion of high thermal conductivity particles inside the fluid is a promising way towards enhancing thermal properties of fluids. The idea of increasing heat transfer in fluids by suspending conductive particles was first addressed by Maxwell (1891). These fluids are termed as *nanofluids* when suspensions of nanometer sized particles are used inside the parent fluid. Nanoparticles stay suspended much longer than micro-particles and, if below a threshold level and/or enhanced with surfactants/stabilizers, remain in suspension almost indefinitely. Furthermore, the surface area per unit volume of nanoparticles is much larger (million times) than that of microparticles (the number of surface atoms per unit of interior atoms of nanoparticles, is very large). These properties can be utilized to develop stable suspensions with enhanced flow, heat-transfer, and other characteristics. Examples of nanofluids are addition of materials such as carbon, copper or copper oxide in liquids such as oil, water, and ethylene glycol.

Nanofluids have attracted great interest recently because of reports of greatly enhanced thermal properties. For example, a small amount (<1% volume fraction) of Cu nanoparticles or carbon nanotubes dispersed in ethylene glycol or oil is reported to increase the inherently poor thermal conductivity of the liquid by 40% and 150%, respectively Choi et al. (2001). Conventional particle-liquid suspensions require high concentrations (>10%) of particles to achieve such enhancement. However, problems of rheology and stability are amplified at high concentrations, precluding the widespread use of conventional slurries as heat transfer fluids. In some cases, the observed enhancement in thermal conductivity of nanofluids is orders of magnitude larger than predicted by well-established theories. Other perplexing results in this rapidly evolving field include a surprisingly strong temperature dependence of the thermal conductivity (Das et al. (2003) and Patel et al. (2003)) and a three-fold higher critical heat flux compared with the base fluids, You et al. (2003) and Vassallo et al. (2004). These enhanced thermal properties are not merely of academic interest. If confirmed and found consistent, they would make nanofluids promising for applications in thermal management. The interdisciplinary nature of nanofluid research presents a great opportunity for exploration and discovery at the frontiers of nanotechnology, Ajayan et al. (2002) and Das et al. (2003).

Experimental Method

Materials Fabrication

The present experimental investigation involves the thermal diffusivity analysis of PAO (poly-alpha-olefin) oil due to the inclusion of three different types of additives: Carbon nanotubes (CNT), Heat treated nanofiber HTT and Exfoliated graphite powder (EXG). CNTs consist of a multiple cylinders of graphite sheets and are approximately 10-15 nm in diameter and were produced by chemical vapor deposition using carbon monoxide and iron cobalt catalyst at temperature between 600 and 800 °C. Carbon nanofibers (HTCNF) were produced through the pyrolysis of carbon-containing gases (methane, ethylene, acetylene, carbon monoxide, etc.) on a metal (most often iron) catalyst at 500-1100°C and then heat treated to 3000 °C. The average diameter is about 100nm. However, the expanded or exfoliated graphite (EXG) was prepared as follow: A mixture containing sulfuric acid and natural graphite was prepared. After 24 hours of reaction, the acid was absorbed by the graphite flakes and then the mixture was filtered, washed with water, and dried. The graphite intercalation compound thus formed was put in an oven at 900°C where rapid expansion occurred. The expansion ratio was as high as 300 times. All nanoparticles were functionalized by adding phenyl and carboxylic groups to facilitate their dispersion in the oil. Then the suspension was shear mixed and sonicated for a period of 1 hour to obtain a well dispersed and stable suspension.

Thermal Measurement

A schematic arrangement of the laser flash (LFA-447) apparatus is shown below, Figure 1.

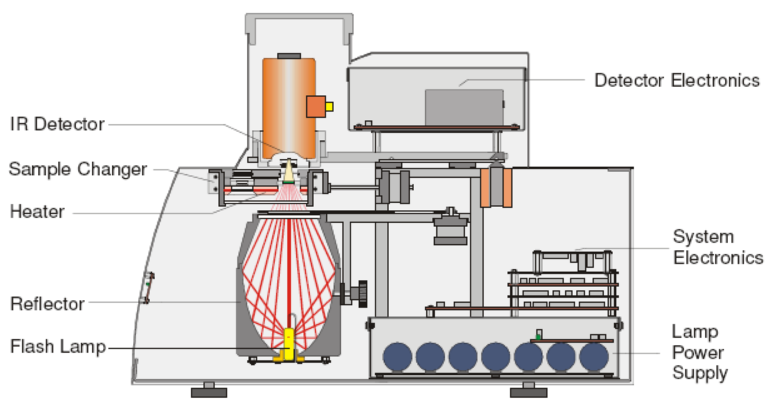

Figure 1. Detailed view of the laser flash apparatus (LFA 447)

The LFA 447 is a modern contact-free laser flash method used for the measurement of thermal diffusivity of both solids and liquids. The thermal diffusivity measuring range is 0.01 to 1000 mm²/s with reproducibility of approximately ± 3%. In addition to the thermal diffusivity, by employing a comparative method, the specific heat can also be determined with this apparatus by using a known sample as the reference. The thermal conductivity range is 0.1 to 2000 W/mK.

The analysis procedure for measuring liquid samples using LFA-447 is slightly different from that followed for a solid sample. The main difference is in the type of sample holder used and the corresponding input data entered in the Nanoflash software.

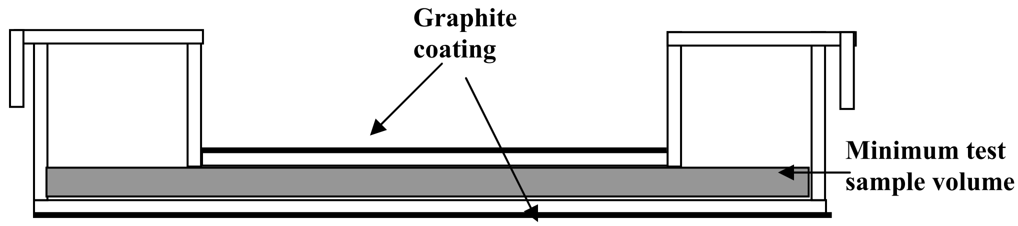

Figure 2. Sample holder for nanofluids thermal diffusivity measurement

To prepare the holder for testing, a thin coating of graphite is sprayed on the bottom of the container and on the top of the lower surface of lid. For the lid a mask is used to prevent coating other surfaces. Accurate values of the density and specific heat of the liquid sample are needed to measure the thermal conductivity of the liquid sample. Now the target sample mass is calculated from the target sample volume and sample density. This target sample mass is now accurately weighed out and poured into the container using a syringe or dropper, Figure 2. Now by using the recommended measurement settings in the Nanoflash software around 8 to 10 measurements are taken for the liquid sample. After measurements are complete, the data is loaded into the LFA analysis software which calculates the thermal diffusivity of the liquid sample. By using a reference liquid sample with known values of thermal-diffusivity, and specific heat the specific heat of the tested sample can be measured.

Experimental results and discussions

Before starting with the measurements for the nanofluid samples, verification of the accuracy of the measurement procedure was carried out by measuring thermal diffusivity of liquid samples like distilled water, ethylene glycol and olive oil and the results were compared with literature. Using the procedure adopted above thermal diffusivity measurements were carried out for the above liquid samples. For all the three samples 10 readings were taken and the average value of the thermal diffusivity (α_s) was obtained in mm^2/sec. From Table 1 it can be seen that a good agreement was observed between the measured values and the values from literature for the three liquid samples. The reproducibility in the thermal diffusivity values for all the three samples was around $\pm$ 2.5 %. All the values for thermal diffusivity were measured around $25 \pm 0.5°C$.

Table 1. Data Comparison between measured and published diffusivities for various liquids

Liquid sample	Present LFA method α_s (mm^2/sec)	Literature α_s (mm^2/sec)	Reference-no
Distilled water	0.1442 ± 0.002	0.1456	45
Ethylene glycol	0.0918 ± 0.001	0.0939	46
Olive oil	0.0881 ± 0.001	0.0799	44,47

After comparison of the LFA technique with literature, the three types of nanofluid samples were then analyzed for their thermal diffusivity and thermal conductivity. As described before all three nanofluid samples CNT, HTT, and EXG were prepared for different loadings of the nanoparticles from 0.1% to 1%. The density of the nanofluid samples corresponding to different loadings were calculated from the rule of mixture. In order to keep the samples well dispersed all three nanofluid samples were kept continuously in the sonic-bath. The three nanofluid samples each with different loading percentage were then analyzed for their thermal diffusivity on the LFA device. For each type of sample total 8 readings were taken and the average value of the thermal diffusivity (α_{av}) was obtained in mm^2/sec. The specific heat of the nanofluid samples was then measured using distilled water as the reference sample. The measured specific heat value was approximately similar to the one calculated from the rule of mixture with an error of $\pm$4%.

The calculated value of density and the measured values of the specific heat and thermal diffusivity were then used to estimate the thermal conductivity of all the nanofluid samples. Table 2 gives the results for the thermal diffusivity and thermal conductivity for the CNT, HTCNF, and EXG nanofluid samples respectively for loading between 0.1 to 1% as compared to the base fluid which is the PAO oil.

Table 2. Percent thermal property enhancement for measured nanofluids

Sample type	**Thermal diff.** (α_{av}) mm^2/sec	**% Increase in** α_{av}	**Thermal cond.** (K) W/mK	**% Increase in** K
PAO Oil	0.2671	--	0.1166	--
		CNT PAO-oil suspensions		
PAO/CNT (0.1%)	0.3230	20.97	0.1558	33.62
PAO/CNT (0.4%)	0.3901	46.10	0.1882	61.38
PAO/CNT (0.8%)	0.5449	104.08	0.2629	125.43
PAO/CNT (1%)	0.6300	135.95	0.3039	**160.63**
		EXG PAO-oil suspensions		
PAO/EXG (0.1%)	0.2890	8.23	0.1377	18.12
PAO/EXG (0.4%)	0.3359	25.80	0.1601	37.29
PAO/EXG (0.8%)	0.4640	73.78	0.2211	89.65
PAO/EXG (1 %)	0.5650	111.61	0.2693	**130.93**
		HTT PAO-oil suspensions		
PAO/HTCNF (0.1%)	0.2740	2.62	0.1290	10.63
PAO/HTCNF (0.4%)	0.3101	16.10	0.1459	25.16
PAO/HTCNF (0.8%)	0.4113	53.93	0.1935	65.94
PAO/HTCNF (1 %)	0.5031	88.38	0.2368	**103.09**

From the above table it can be seen that as the percentage of volume of nanoparticles was increased for all the three types of nanofluids effective thermal conductivity showed in increase. The maximum value of percentage enhancements for the CNT, EXG, and HTCNF nanoparticle-oil suspensions were 160.63%, 130.93%, and 103.09% respectively corresponding to 1% volume of the nanoparticles. Among all three types of nanofluids, the CNT based nanoparticle-oil suspension had the greatest enhancement (160.63%). This result for the CNT-oil suspension is similar to that observed by Eastman et al. (2001). They noted an enhancement of 160 % for the CNT-oil suspension for oil with thermal conductivity of 0.1448 W/mK.

It was interpreted that the maximum percentage enhancement obtained for the CNT based nanofluid was due to the better mixing of the carbon nanotubes in the PAO oil. The visual of all the three types of nanofluids clearly revealed that the carbon nanotubes were well dispersed in the oil as compared to the exfoliated graphite and heat treated nanofiber particles. Also the other important reason can be the higher thermal conductivity of the CNT as compared to EXG, and HTCNF nanoparticles.

Theoretical Model

The idea for the formulation of a theoretical model for the effective thermal conductivity of nanoparticle suspensions was established after observing the micrographs of well dispersed suspensions of nanoparticles in different basefluids. Figure 3** shows a TEM micrograph of nanoparticle suspension. From the figure it can be observed that an aggregate of nanoparticles form a foam type network for the two phase dispersion of nanoparticles in the base fluid.

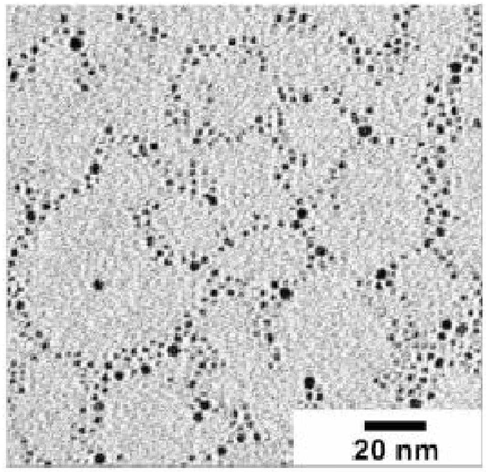

Figure 3. TEM micrograph for nanoparticle arrangement in base fluid

From this and other observations found in literature for the different micrographs of the nanoparticle-fluid suspensions it was considered that formation of this foam type structure wherein the nanoparticles are interconnected into a network type arrangement of number of cells, can be a possible reason for the high value of thermal conductivity of the nanoparticle-fluid suspensions. In order to investigate this theoretically we made a broad assumption regarding the arrangement of nanoparticles in the base fluid. Figure 4 shows an enlarged view of a single cell which is assumed to have a hexagonal geometry with nanoparticles aggregates forming the sides and corners of the hexagon. The effective thermal conductivity values of the three types of nanoparticle suspensions to be studied here consisted of CNT, EXG, and HTCNF based nanoparticle-PAO oil suspensions as described in the previous section.

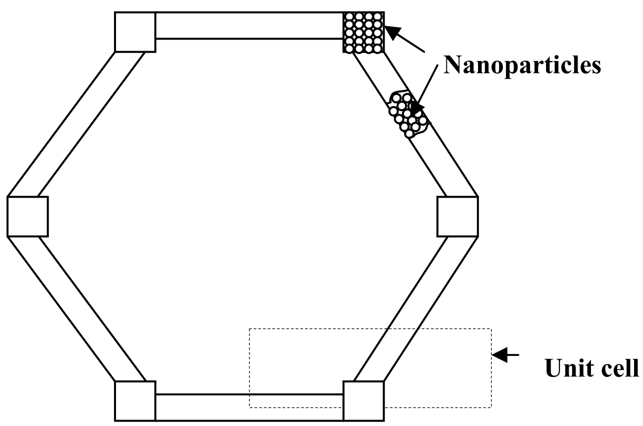

Figure 4. Model domain showing hexagonal form of nanoparticles network in base fluid

Now by considering one-dimensional heat conduction as taken by Calmidi and Mahajan (1999) and applying the series law of thermal resistances to the unit cell representation as shown in Figure 5 below, the equation for effective conductivity of the nanofluid is derived by following the same steps as adopted by Calmidi and Mahajan (1999). The solid volume fraction which is basically the percent volume of nanoparticles in the fluid was calculated as the ratio of volume of nanoparticles to the volume of the unit cell.

**Choi SUS, www.eere.energy.gov/vehiclesandfuels/ pdfs/hvso_2006/13_choi.pdf .

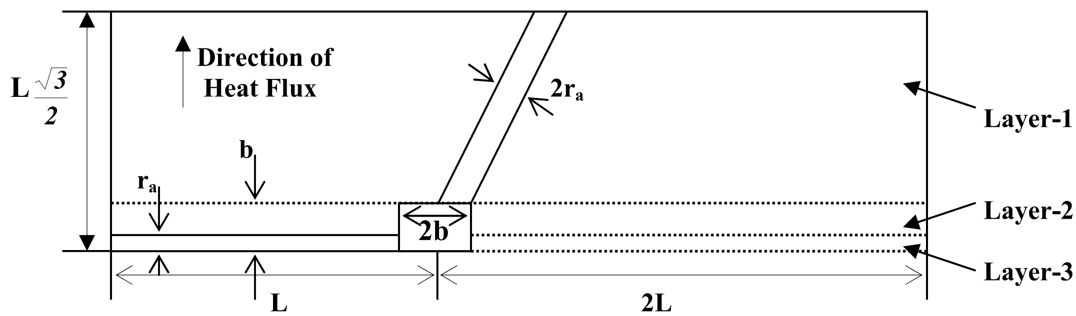

Figure 5. Unit cell representation showing three layers in a series arrangement

The unit cell in Figure 5 is divided into three layers and the thermal conductivity of each layer is calculated based on the volume ratio between the solid and the fluid phases.
The general equation for thermal conductivity of each layer is given by,

$$K_i = \frac{V_{si}}{V_{Ti}} K_s + \frac{V_{fi}}{V_{Ti}} K_f \tag{1}$$

where K_s is the thermal conductivity of the solid which is the nanoparticle aggregate, K_f is the thermal conductivity of the fluid phase which is the PAO oil, K_i is the thermal conductivity of the ith layer and V_{si}, V_{fi}, and V_{Ti} are the solid, fluid, and total volumes for the respective layer.
Thus the equations for thermal conductivity of each layer is given by,

Layer-1:
$$K_1 = K_f + \frac{(K_s - K_f)}{3}\left(1 + \frac{b}{L}\right) \tag{2}$$

Layer-2:
$$K_2 = K_f + \frac{2}{3}(K_s - K_f)\left(\frac{b}{L}\right) \tag{3}$$

Layer-3:
$$K_3 = K_f + \frac{4}{3\sqrt{3}}(K_s - K_f)\left(\frac{r_a}{L}\right) \tag{4}$$

In Eq. 4 the area ratio c is defined as,

$$c = \frac{r_a}{b} \tag{5}$$

The effective thermal conductivity of the unit cell is now calculated by combining all the layers together in series as,

$$\frac{\sum_{i=1}^{3} L_i}{K_{eff}} = \sum_{i=1}^{3} \frac{L_i}{K_i} \tag{6}$$

Where K_{eff} is the effective thermal conductivity of the unit cell and L_i is height of the ith layer. The solid volume fraction which is the volume fraction of the nanoparticles X_n is the ratio of solid volume to the volume of unit cell. For the assumed hexagonal geometry it was obtained as,

$$X_n = \frac{r_a(L+b) + (b - r_a)2b + (L\frac{\sqrt{3}}{2} - b)\frac{4r_a}{\sqrt{3}}}{3L\left(L\frac{\sqrt{3}}{2}\right)} \tag{7}$$

By substituting for r_a from Eq. 5 the resulting quadratic equation for ratio b/L was obtained as,

$$\frac{b}{L} = \frac{-c + \sqrt{c^2 + \frac{2}{\sqrt{3}}(X_n)\left(2 - c\left(1 + \frac{4}{\sqrt{3}}\right)\right)}}{\frac{2}{3}\left(2 - c\left(1 + \frac{4}{\sqrt{3}}\right)\right)} \tag{8}$$

By combining Eqs. 2, 3,4,5 & 6 the equation for effective thermal conductivity of the unit cell was obtained as,

$$K_{eff} = \left\{\left(\frac{2}{3}\right)\left(\frac{c\left(\frac{b}{L}\right)}{K_f + \left(1 + \frac{b}{L}\right)\frac{(K_s - K_f)}{3}} + \frac{(1-c)\left(\frac{b}{L}\right)}{K_f + \frac{2}{3}\left(\frac{b}{L}\right)(K_s - K_f)} + \frac{\left(\frac{\sqrt{3}}{2} - \frac{b}{L}\right)}{K_f + \frac{4c}{3\sqrt{3}}\left(\frac{b}{L}\right)(K_s - K_f)}\right)\right\}^{-1} \tag{9}$$

Using Eq. 8 & 9 the effective thermal conductivity of the nanofluid can be obtained in terms of the volume fraction of nanoparticles 'Xn' and the area ratio 'c'. The thermal conductivity of the nanoparticle aggregate K_s was estimated by using the rule of mixture by assuming that the corner and the edges of the foam network shown in Figure 4 consisted of nanoparticles with interfacial contact and surrounded by the PAO oil.

The thermal conductivity of nanoparticles was taken as 2000 W/mK for CNT, 1700 W/mK for EXG and 1300 W/mK for the HTCNF respectively. Now in order to obtain a fit between the experimentally determined effective thermal conductivity values and the predicted values from Eq. 9 first the value for area ratio 'c' was determined. For each type of nanofluid corresponding to 0.1 percent volume fraction of nanoparticles the value area ratio 'c' was determined such that the predicted value of thermal conductivity ratio (K_{eff}/K_f) from Eq. 8 matched with the experimental measured value. The area ratio 'c' thus determined for each type of nanofluid for 0.1 percent volume fraction was then used to estimate the values of (K_{eff}/K_f) for different volume fraction of nanoparticles from 0.2 to 1 percent. The results for the comparison between the predicted values of (K_{eff}/K_f) for the three fluids with their experimental values were plotted as shown in Figure 6.

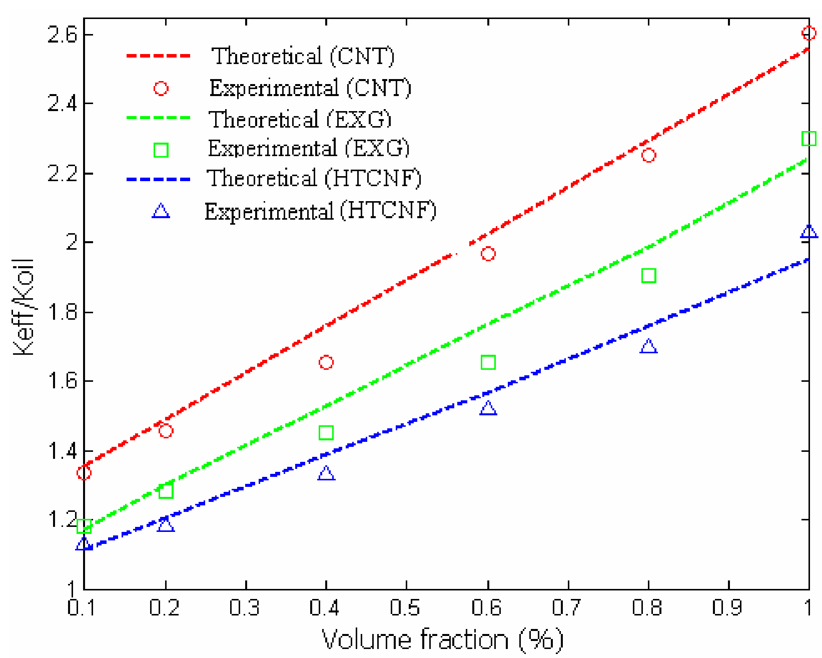

Figure 6. Predictions of the theoretical model for thermal conductivity ratio of CNT, EXG and HTCNF based nanofluids as compared with experimental results

From the Figure 6 it can be observed that the theoretical model slightly overestimates the values of effective thermal conductivity for all three types of fluids (except for 1% volume fraction loading).

However, a very reasonable agreement was obtained between the experimentally measured values and that predicted by the numerical model. Thus, even though the theoretical model was formulated based on a broader assumption regarding the foam type arrangement of nanoparticles network, its satisfactory outcome explains that the anomalous values of thermal conductivity of the nanoparticle based fluids can be possibly due to the high thermal conductivity heat transfer path provided by this type of arrangement. This high conductivity path results in an efficient flow of heat through the base fluid and thereby enhancing the overall effective thermal conductivity of the nanoparticle suspension.

Conclusions

A detailed study was carried to out to analyze the effective thermal conductivity of nanoparticle-PAO-oil suspensions with three types of nanoparticles namely CNT, EXG, and HTCNF. The study included the use of a modern light flash technique to measure the thermal conductivity of the three nanofluids with different nanoparticle loadings. The results obtained were similar to that observed in literature for experimentally measured thermal conductivity values of nanofluids. The percent enhancement in the thermal conductivity of the three nanofluids over the PAO-oil was maximum for the CNT based nanoparticle suspension followed by the EXG and HTCNF. A theoretical model based on a novel point of view regarding the arrangement of nanoparticles in the base fluid was formulated for the effective thermal conductivity of nanofluids. The predictions from the theoretical model showed a reasonable agreement with the experimental values which can basically open the possibility of a new discussion for the theory behind the anomalous thermal properties of the nanofluids observed in literature.

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