International Journal of Nanoelectronics and Materials

In Press, Accepted Manuscript – Note to user

Volume fraction effects on thermophysical properties of Fe_3O_4/MWCNT Based Hybrid Nanofluid

Sumbul Purree[1], Muhammad Nadeem[1,*], Azeem shahzad[1], Muhammad Zubair[2], Muhammad Saeed Akhtar[3], Muhammad Khalid[4], Imran Sadiq[5], Hasan Mehmood Khan[6], Sarwat Zahra[3]

[1]Department of Basic Sciences, University of Engineering and Technology, Taxila, 47056, Pakistan
[2]Department of Mechanical and Nuclear Engineering, University of Sharjah, 27272. Sharjah. UAE
[3]Division of Science and Technology, University of Education, College Road, Township, Lahore, 54770, Pakistan
[4]Department of Physics, University of Karachi, Karachi, 75270, Pakistan
[5]Centre of Excellence in Solid State Physics, University of the Punjab, Lahore, Pakistan
[6]Department of Physics, The Islamia University of Bahawalpur, 63100, Pakistan

Received 18 Dec 2020, Revised 31 December 2020, Accepted 14 January 2021

Abstract: In this work, Polyalphaolefin oil-based hybrid nanofluid containing Fe_3O_4/MWCNT nanocomposite has been prepared to consider the impact of volume fraction on thermal conductivity through graphical representation. The heat transfer of the prepared nanofluids is investigated via. adjusting the surface morphology, molar ratios and size of the nanocomposite. Phase and composition of the synthesized sample was inspected through XRD and FTIR spectroscopy. The average crystallite size was observed to be 7.74 nm from Debye-Scherrer equation. Thermophysical parameters such as diffusivity, specific heat and thermal conductivity were measured through transient plane source method. The sample showed 2% enhancement in thermal conductivity with addition of nanocomposite as compared to pure polyalphaolefin oil for 0.7 wt.% at 50°C and this value declined when shifted towards very high temperatures. Similarly, thermal diffusivity and specific heat also showed a linear trend as a function of volume fraction. This shows that the prepared nanofluid contains high stability and thermal conductivity as compared to conventional lubricant (i.e., PAO) and has potential in heat transfer applications as a lubricant and heat transfer fluid.

Keywords: Thermal conductivity, diffusivity, volume fraction, crystallite size etc.

1. INTRODUCTION

Highly efficient heat transfer plays a vital role on shelf life and effective performance of electronic devices. However, conservative fluids have very low thermal performance and there arises a need to develop such fluids which have high thermal conductivity. For this, the field of nanofluid has gained a rapid interest and it has been reported that nanofluids have ultra-high thermal performance as compared to conventional coolants which makes them favorable for many thermal applications. Nanofluids are colloidal suspensions with nanometer sized solid particles suspended into fluids i.e., water, ethylene glycol and oils etc. [1]. Addition of nanosized solid particles like Cu [2], Ag [3], Fe_3O_4, Fe_2O_3 [4], Al_2O_3, TiO_2 and graphene etc. boost the thermal conduction and convection of the basefluid [5]. Amidst these fluids, Fe_3O_4 nanofluids show high

---

[*] Corresponding author: e-mail: badaninadeem@gmail.com
Postal Address: Dr. Muhammad Nadeem, Assistant professor, Department of Basic Sciences and Humanities, University of Engineering and Technology, 47056, Taxila.

convection rates as compared to other heat transfer fluids due to its exceptional magnetic properties along with high thermal efficiency [6].

Although ferrofluids have displayed enormously exciting potential applications, some vital hinders such as the low stability of nanofluids [7], high viscosity [8, 9], rise in pressure losses and pumping power [10], agglomeration due to nanoparticles shape and size [11, 12], inconsistency in theoretical and experimental data [13], cost and polydispersity of nanoparticle still exist before commercialization of nanofluids [10, 14-19]. Among these issues, viscosity of ferrofluids is the most important and challenging concern because pumping power, pressure drop, and convective heat transfer has a strong dependence upon the viscosity of nanofluids [20]. Consequently, effective viscosity analysis requires more attention for the complete understanding of thermal transport of nanofluids to break through from the hurdles restricting its commercialization [17]. A lot of research has been done on nanofluids for the past few years and it has been observed that concentration of nanoparticles in the basefluid has direct impact on the viscosity of nanofluids i.e., increasing the volume fraction may increase the viscosity [21-23]. To resolve this matter, several techniques like polymer coating and addition of chain like structures (carbon nanotubes) [24] has been employed and studied but no effective method to manufacture a less viscous nanofluid with high stability and thermal conductivity is developed to this day.

In literature, the properties of various basefluids studied by researchers were carefully examined and it was observed that the thermal conductivity of poor heat transfer basefluids is good as compared to fluids with better heat transfer rates e.g. water [25, 26]. This indicates that the oils can be considered a good choice as a basefluid, but they have high viscosity limiting their use as basefluid in synthesis of nanofluids. Amidst oils, polyalphaolefin oil has special importance as it exhibits better thermal stability as a coolant in radar systems and the viscosity of polyalphaolefin oil reduces at high temperatures [27, 28]. Thus, use of polyalphaolefin oil as a basefluid along with aforementioned techniques, to reduce the viscosity and enhance the thermal conductivity and stability, in the fabrication of nanofluids can be considered an excellent option.

The aim of this article is to fabricate a highly stable oleic acid coated Fe_3O_4 grafted with MWCNTs based nanocomposite and its colloidal suspension in polyalphaolefin oil as a basefluid to enhance the thermal conductivity and high light its potential in heat transfer applications.

2. METHODS AND MATERIALS

2.1 Chemicals

All the chemicals, Ferrous Chloride ($FeCl_2$), Ferric Chloride ($FeCl_3$), Ammonium hydroxide (NH_4OH with 32% ammonia), hydrochloric acid (HCl), Deionized water, Multiwalled Carbon Nanotubes (MWCNT), oleic acid, o-xylene and polyalphaolefin oil (PAO) are acquired (purchased) in Pakistan. All these reagents were analytical grade and were used without further purification.

2.2 Synthesis of Iron oxide nanoparticles

Iron oxide nanoparticles were produced by chemical co-precipitation method. First, 0.5M of $FeCl_2.4H_2O$ and 0.79M of $FeCl_3.6H_2O$ solutions in distilled water were prepared and mixed under constant stirring at 40°C for half hour. 35ml of ammonium hydroxide was added drop by drop to the above solution to adjust the pH at 11 and initiate the formation of precipitates. The solution was stirred at 1000rpm, 40°C temperature for 20 minutes. The formation of black precipitates indicates the nucleation growth of iron oxide nanoparticles. Then, the black precipitates were separated via. centrifugation and were washed several times with distilled water to remove residuals. At last, the obtained nanoparticles were dried in oven at 40°C temperature for 24 hours.

2.3 Oleic Acid Coating

Physical immobilization method was used to cap oleic acid on previously prepared nanoparticles. 5% (w/v) of iron oxide nanoparticles were added to 45ml (v/v) oleic acid solution. The solution was stirred rigorously at 40°C for one hour and then, washed four to five times with acetone and dried in oven.

2.4 Fe_3O_4/MWCNT Nanocomposite

Solution blending method was used to fabricate the Fe_3O_4/MWCNT nanocomposite which is hydrophilic in nature. Oleic acid coated iron oxide nanoparticles were blended with Multiwalled carbon nanotubes (MWCNT) with 50 (w/w) % in 10% (v/v) oleic solution during continuous stirring of 1100rpm at constant temperature for 1 hour. Then, the solution was sonicated for 2 hours at 40°C temperature. The obtained composite was washed with acetone several times and dried in oven for 15 hours. Finally, the sample was grounded into fine powder for further characterization.

2.5 Preparation of Nanofluid

Nanofluid was synthesized by suspending nanocomposite with all three different compositional ratios in three different volume concentration of 0.3 wt. %, 0.5 wt.% and 0.7 wt.% in polyalphaolefin basefluid. The volume fraction of these solutions was calculated by formula:

$$\boldsymbol{\phi} = \frac{\left(\frac{\boldsymbol{W_{Nanocomposite}}}{\boldsymbol{\rho_{Nanocomposite}}}\right)}{\left[\left(\frac{\boldsymbol{W_{Nanocomposite}}}{\boldsymbol{\rho_{Nanocomposite}}}\right)+\left(\frac{\boldsymbol{W_{Polyalphaolefin}}}{\boldsymbol{\rho_{Polyalphaolefin}}}\right)\right]} \times \mathbf{100}$$

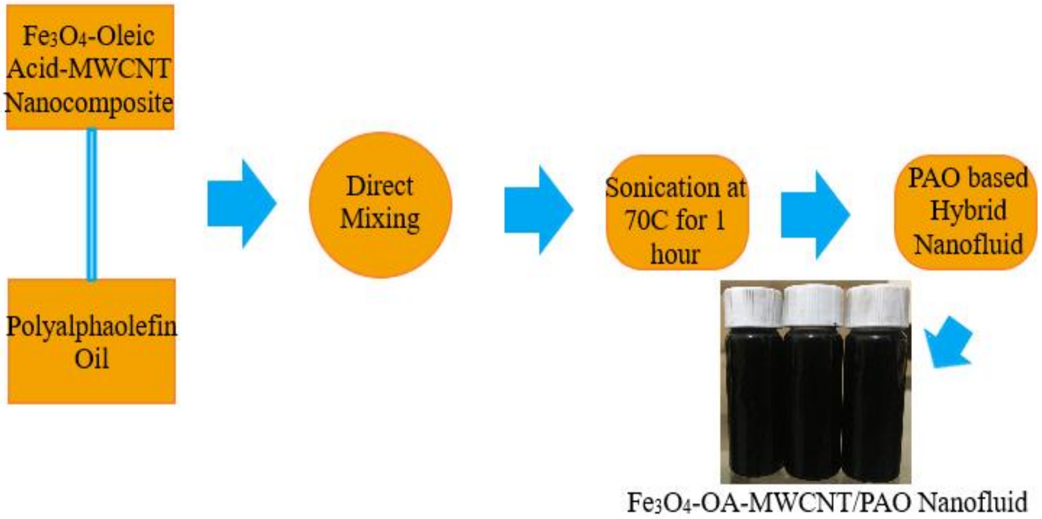

Figure 1: Flow diagram of preparation of PAO based nanofluid

The above solutions were sonicated for 1 hour at 70°C temperature. The obtained nanofluids were then used for further characterization.

3. CHARACTERIZATION

X-ray diffractometer of Bruker D8 Advance Diffractometer with copper tube ($\lambda = 1.5406A$) was used for the phase identification of samples with average range $20^{\circ}\ to\ 80^{\circ}$ along with LYNXEYETM detector. Perkin-Elmer double beam spectrophotometer with 0.5 cm^{-1} resolution was used to record the IR absorption spectrum of already prepared nanocomposite at room temperature. The range of absorption spectrum used in this analysis is 399.193 to 4000 cm^{-1}. Hot disc transient plane source technique was used to calculate the thermophysical parameters of the two given samples (Fe_3O_4@MWCNT/PAO nanofluid and polyalphaolefin oil). Thermal Constant analyzer equipment was used to obtain the experimental data and the equipment was calibrated three times. The temperature range used for calculation was 50-100°C. About three measurements were taken for about 4 hours with 25 °C intervals in between each measurement. The process was repeated several times to ensure the validity of the results.

4. RESULT AND DISCUSSIONS

4.1. Phase Identification

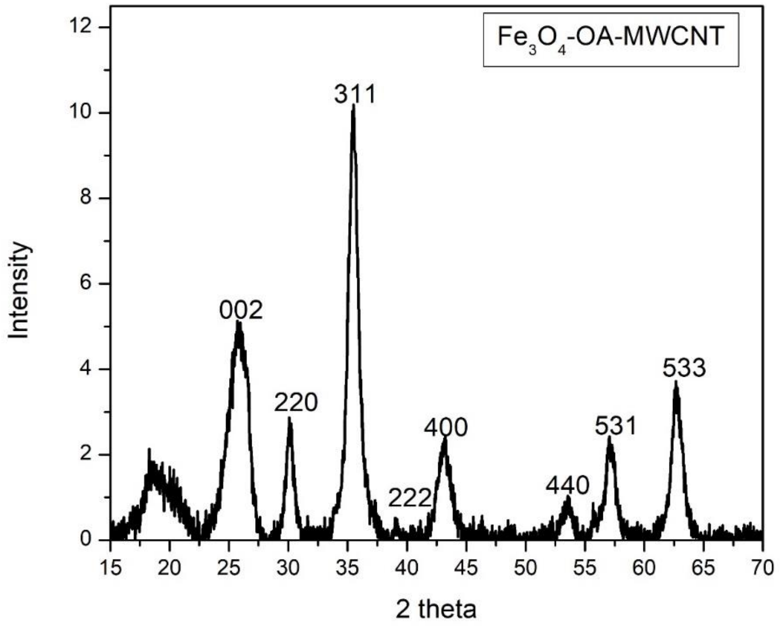

Figure 2: XRD spectrum of Fe_3O_4-OA-MWCNT based nanocomposite

Figure 2 represents the XRD spectrum ofFe_3O_4-OA-MWCNT nanocomposite. The curve shows the X-ray diffraction from (220), (311), (222), (400), (440), (511), (531) and (533) planes corresponding to 2θ diffraction angles at $30^{\circ}, 35^{\circ}, 38^{\circ}, 43^{\circ}, 53.9^{\circ}, 53.4^{\circ}, 57^{\circ}$ and 62° of the crystal lattice. The reflecting planes confirms the presence of Fe_3O_4 phase of iron when compared to JCPDs card no. 41-1487, as lattice planes (210), (300) and (320) are absent which are characteristic planes of maghemite [29]. The reflecting plane (002) at the angle 25.9° represents the sheets of graphene stacked together and when compared to JCPDs card no. 41-1487 confirms the presence of MWCNT in the composite [30]. The sharpness of these peaks' points to crystalline behavior of the sample. The crystallite size was calculated using Debye-Scherrer formula:

$$L_{hkl} = \frac{0.94\lambda}{\beta \cos\theta} \qquad (4.1)$$

Where, $L_{hkl}, \beta, \lambda, \theta$ corresponds to crystallite size, full wave half maximum, wavelength and diffraction angle. The crystallite size of the given nanocomposite was determined to be 7.74 nm.

4.2. Compositional analysis

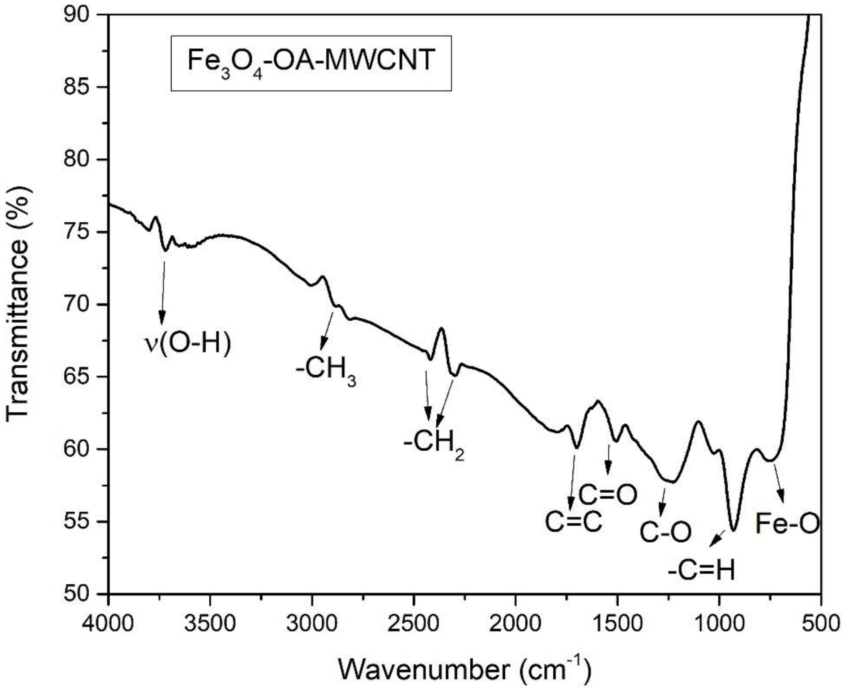

Figure 3: FTIR spectrum of Fe_3O_4/OA/MWCNT nanocomposite

Figure 3 illustrates the FTIR spectrum of Fe_3O_4-OA-MWCNT nanocomposite. The absorption at 929.9 cm^{-1} is because of bending of =C-H bond. The peak at 740.6 cm^{-1} wavenumber shows the stretching vibration of metallic bond i.e., Fe-O which is slightly deviated to 551 cm^{-1} due to oleic acid coating on the IONPs. The existence of C=C bond is indicated through peaks at 1505.41-1695.55 cm^{-1} directing towards the tubule like structures of graphene sheets/MWCNT. This peak is weak because of large number of asymmetrical carbons. From 2500 cm^{-1} to 2900 cm^{-1} two absorption peaks are due to asymmetric stretching vibration of -CH2 and -CH3 bonds. O-H bond stretching vibrations was also observed through a very small peak around 3800 cm^{-1} wavenumber value.

4.3. Thermophysical Properties

Thermal and Physical properties of Fe_3O_4-MWCNT/PAO based nanofluid was studied by investigating the thermal conductivity, thermal diffusivity and specific as a function of temperature and volume fraction to delve into its potential as a heat transfer lubricant.

Thermal conductivity of oleic acid coated Fe_3O_4 blend with MWCNT dispersed in polyalphaolefin oil was measured in three different volume fractions of 0.3 wt.%, 0.5 wt.% and 0.7 wt.% at temperature range of 50-100 °C. For heat transfer performance of nanofluids, conduction behavior of nanofluids must be evaluated. Nanoparticles act as liquid molecules in the basefluid due to their large surface to volume ratios and very minute sizes. Consequently, nanoparticles are a key to improve the thermal capability of conventional fluids.

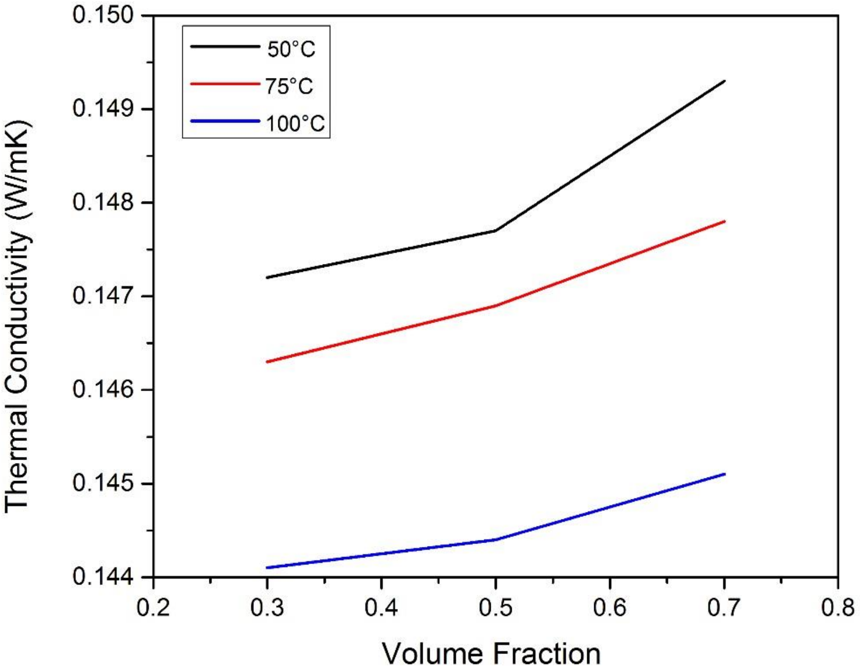

Figure 4 Thermal conductivity of Fe_3O_4/MWCNT/PAO nanofluid as a function of volume fraction

Figure 4 shows the thermal conductivity as a function of volume fraction at three different temperatures (i.e., 50-100 °C). It can be clearly seen that thermal conductivity of nanofluid rises by increasing the volume fraction. This is because of the rise in Brownian motion due to enhanced aggregation and interaction of particles. The resulting collision among particles helps provides a new heat conduction route in the system. The linear reduction in thermal conductivity of Fe_3O_4-MWCNT/PAO based nanofluid was observed with increasing temperature due to decline in viscosity of basefluid at high temperature values and viscosity of nanofluid is closely related to thermal conduction. However, the thermal conductivity when compared to pure basefluid is still very high (2% enhancement at 0.7 wt.%) which clearly points towards the potential of Fe_3O_4-MWCNT nanocomposite in PAO basefluid for heat transfer applications.

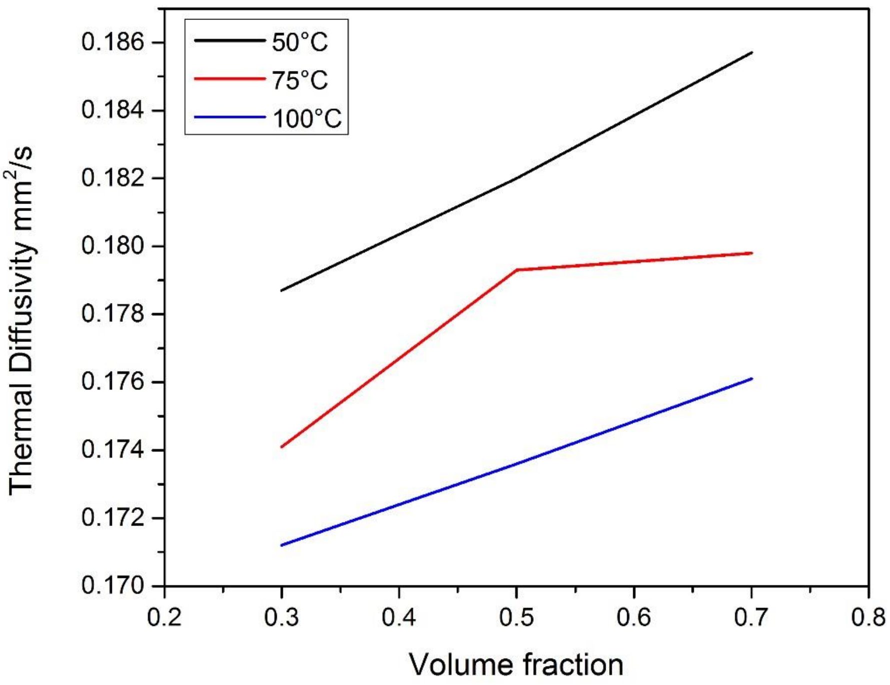

Figure 5 Thermal diffusivity of Fe_3O_4/MWCNT/PAO nanofluid as a function of volume fraction

Figure 5 shows the thermal diffusivity as a function of temperature and volume fraction of Fe_3O_4-MWCNT/PAO nanofluid at 0.3 wt.%, 0.5 wt.%, 0.7 wt.%, respectively, and its comparison with pure polyalphaolefin oil. Thermal diffusivity declined as the temperature was increased as shown in the graph, but the curves shift to high values when volume concentration of nanocomposite was enhanced in the lubricant. This points towards the enhancement in the thermal diffusivity of the sample with low thermal diffusivity (i.e., PAO). The ability to transport heat comparative to storing thermal energy can be described by thermal diffusivity. The high thermal diffusivity has a direct relation to thermal conductivity. The high diffusivity was observed at 0.7 wt.% and low diffusivity was observed at 0.5 wt.%. This deviation from normal trend is caused by high aggregation time which resulted in cluster formation obstructing the conduction path.

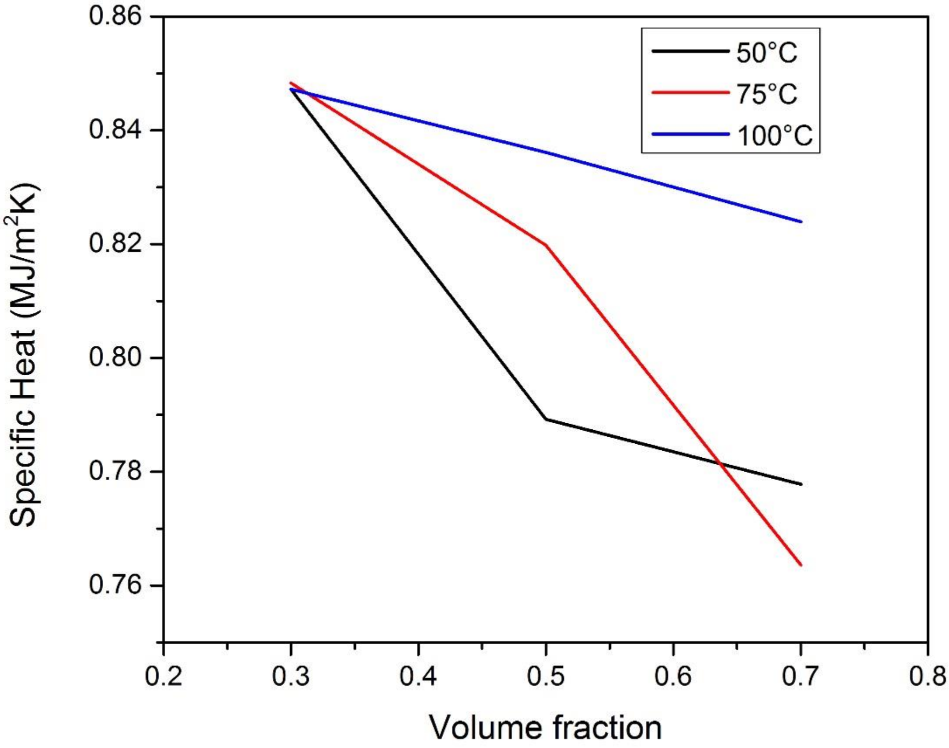

Figure 6 Specific heat of Fe_3O_4/MWCNT/PAO nanofluid as a function of volume fraction

Figure 6 shows the specific heat trend of Fe_3O_4-MWCNT nanocomposite based nanofluid at various volume concentration. The result shows that the specific heat value is decreased by increasing the volume fraction. This is due to highly complex interaction among solid particles of the nanocomposite and molecules of basefluid at the interface. Also, heat transfer was increased due to ordered structure of nanoparticles among liquid molecules and this provided a path for heat conduction. In other words, the amount of stored energy is decreased, and convection is increased when concentration of nanocomposite in PAO basefluid was increased.

5. CONCLUSION

Fe_3O_4-MWCNT /PAO based nanofluid was successfully synthesized via simple and efficient techniques (i.e., in-situ polymerization and two step approach). XRD investigation exhibited the crystal nature and small size of 7.74 nm of the prepared sample. The addition of Fe_3O_4-MWCNT nanocomposite in the basefluid successfully enhanced the thermal conductivity of PAO lubricant. Furthermore, the thermal conductivity was clearly dependent on volume fraction of particles and 2% enhancement was observed at 0.7 wt.% of nanocomposite in the basefluid. However, this value declined when temperature shifted to very high values. The particle concentration also has a significant effect on the heat capacity of the nanofluid. The Fe_3O_4-MWCNT/PAO nanofluid has a great potential in various fields for heat removal and as a heat efficient lubricant.

6. REFERENCES

[1] N. Ali, J. A. Teixeira, and A. Addali, "A review on nanofluids: fabrication, stability, and thermophysical properties," *Journal of Nanomaterials*, vol. 2018, 2018.

[2] A. Dogonchi, M. Hashemi-Tilehnoee, M. Waqas, S. M. Seyyedi, I. Animasaun, and D. Ganji, "The influence of different shapes of nanoparticle on Cu–H2O nanofluids in a partially heated irregular wavy enclosure," *Physica A: Statistical Mechanics and its Applications,* vol. 540, p. 123034, 2020.

[3] S. Sridhar, R. Karuppasamy, and G. Sivakumar, "Experimental Investigation of Heat Transfer Enhancement of Shell and Tube Heat Exchanger Using SnO2-Water and Ag-Water Nanofluids," *Journal of Thermal Science and Engineering Applications,* vol. 12, 2020.

[4] S. Banerjee, "Basics and Applications of Ferrofluids," in *Handbook of Research on Developments and Trends in Industrial and Materials Engineering*, ed: IGI Global, 2020, pp. 366-400.

[5] H.-H. Ting and S.-S. Hou, "Numerical Study of Laminar Flow Forced Convection of Water-Al2O3 Nanofluids under Constant Wall Temperature Condition," *Mathematical Problems in Engineering,* vol. 2015, 2015.

[6] A. Banisharif, M. Aghajani, S. Van Vaerenbergh, P. Estellé, and A. Rashidi, "Thermophysical properties of water ethylene glycol (WEG) mixture-based Fe3O4 nanofluids at low concentration and temperature," *Journal of Molecular Liquids,* p. 112606, 2020.

[7] M. Imran, A. H. Shaik, A. R. Ansari, A. Aziz, S. Hussain, A. F. F. Abouatiaa, A. Khan, and M. R. Chandan, "Synthesis of highly stable γ-Fe 2 O 3 ferrofluid dispersed in liquid paraffin, motor oil and sunflower oil for heat transfer applications," *RSC advances,* vol. 8, pp. 13970-13975, 2018.

[8] A. Zareie and M. Akbari, "Hybrid nanoparticles effects on rheological behavior of water-EG coolant under different temperatures: An experimental study," *Journal of Molecular Liquids,* vol. 230, pp. 408-414, 2017.

[9] V. Sridhara and L. N. Satapathy, "Al 2 O 3-based nanofluids: a review," *Nanoscale research letters,* vol. 6, p. 456, 2011.

[10] N. K. Gupta, A. K. Tiwari, and S. K. Ghosh, "Heat transfer mechanisms in heat pipes using nanofluids–A review," *Experimental Thermal and Fluid Science,* vol. 90, pp. 84-100, 2018.

[11] H. Xie, W. Yu, and W. Chen, "MgO nanofluids: higher thermal conductivity and lower viscosity among ethylene glycol-based nanofluids containing oxide nanoparticles," *Journal of Experimental Nanoscience,* vol. 5, pp. 463-472, 2010.

[12] A. Joseph, J. Fal, G. Żyła, and S. Mathew, "Nanostructuring of 1-butyl-4-methylpyridinium chloride in ionic liquid–iron oxide nanofluids," *Journal of Thermal Analysis and Calorimetry,* pp. 1-8, 2018.

[13] J. Wells, O. Kazakova, O. Posth, U. Steinhoff, S. Petronis, L. K. Bogart, P. Southern, Q. Pankhurst, and C. Johansson, "Standardisation of magnetic nanoparticles in liquid suspension," *Journal of Physics D: Applied Physics,* vol. 50, p. 383003, 2017.

[14] K. Khanafer and K. Vafai, "A review on the applications of nanofluids in solar energy field," *Renewable Energy,* vol. 123, pp. 398-406, 2018.

[15] J. R. Eggers and S. Kabelac, "Nanofluids revisited," *Applied Thermal Engineering,* vol. 106, pp. 1114-1126, 2016.

[16] D. Dey, P. Kumar, and S. Samantaray, "A review of nanofluid preparation, stability, and thermo-physical properties," *Heat Transfer—Asian Research,* vol. 46, pp. 1413-1442, 2017.

[17] M. Gupta, V. Singh, R. Kumar, and Z. Said, "A review on thermophysical properties of nanofluids and heat transfer applications," *Renewable and Sustainable Energy Reviews,* vol. 74, pp. 638-670, 2017.

[18] W. Chamsa-ard, S. Brundavanam, C. Fung, D. Fawcett, and G. Poinern, "Nanofluid types, their synthesis, properties and incorporation in direct solar thermal collectors: A review," *Nanomaterials,* vol. 7, p. 131, 2017.

[19] D. K. Devendiran and V. A. Amirtham, "A review on preparation, characterization, properties and applications of nanofluids," *Renewable and Sustainable Energy Reviews*, vol. 60, pp. 21-40, 2016.

[20] A. A. Nadooshan, H. Eshgarf, and M. Afrand, "Measuring the viscosity of Fe3O4-MWCNTs/EG hybrid nanofluid for evaluation of thermal efficiency: Newtonian and non-Newtonian behavior," *Journal of Molecular Liquids*, vol. 253, pp. 169-177, 2018.

[21] S. P. Jang, J.-H. Lee, K. S. Hwang, and S. U. Choi, "Particle concentration and tube size dependence of viscosities of Al 2 O 3-water nanofluids flowing through micro-and minitubes," *Applied Physics Letters*, vol. 91, p. 243112, 2007.

[22] P. Phong, P. Nam, N. Phuc, B. Huy, L. Lu, D. Manh, and I.-J. Lee, "Effect of Zinc Concentration on the Structural, Optical, and Magnetic Properties of Mixed Co-Zn Ferrites Nanoparticles Synthesized by Low-Temperature Hydrothermal Method," *Metallurgical and Materials Transactions A*, vol. 50, pp. 1571-1581, 2019.

[23] A. Naddaf and S. Z. Heris, "Density and rheological properties of different nanofluids based on diesel oil at different mass concentrations," *Journal of Thermal Analysis and Calorimetry*, vol. 135, pp. 1229-1242, 2019.

[24] B. Alemour, M. Yaacob, H. Lim, and M. R. Hassan, "Review of Electrical Properties of Graphene Conductive Composites," *International Journal of Nanoelectronics & Materials*, vol. 11, 2018.

[25] G. Żyła and J. Fal, "Experimental studies on viscosity, thermal and electrical conductivity of aluminum nitride–ethylene glycol (AlN–EG) nanofluids," *Thermochimica Acta*, vol. 637, pp. 11-16, 2016.

[26] X. Wang, J. Zhang, M. Yin, G. Wang, J. Han, M. Dai, and Z. Sun, "A comprehensive review on the properties of nanofluid fuel and its additive effects to compression ignition engines," *Applied Surface Science*, vol. 504, p. 144581, 2020.

[27] L. Wu, Y. Zhang, G. Yang, S. Zhang, L. Yu, and P. Zhang, "Tribological properties of oleic acid-modified zinc oxide nanoparticles as the lubricant additive in poly-alpha olefin and diisooctyl sebacate base oils," *RSC Advances*, vol. 6, pp. 69836-69844, 2016.

[28] S. Choi, Z. Zhang, W. Yu, F. Lockwood, and E. Grulke, "Anomalous thermal conductivity enhancement in nanotube suspensions," *Applied physics letters*, vol. 79, pp. 2252-2254, 2001.

[29] Y. Y. BYONG and K. SEUNG-YEOP, "Assembly of Magnetite Nanoparticles into Spherical Mesoporous Aggregates with a 3-D Wormhole-Like Porous Structure," *J. Mater. Chem*, pp. 1-9, 2010.

[30] H. Xiong, L. Wang, S. U. Rehman, Y. Chen, Q. Tan, L. Zhang, Q. Huang, F. Wu, J. Yang, and Z. Zhong, "Carbon coated core-shell FeSiCr/Fe3C embedded in carbon nanosheets network nanocomposites for improving microwave absorption performance," *NANO*, 2020.