



TECHNICAL UNIVERSITY OF CLUJ-NAPOCA

ACTA TECHNICA NAPOCENSIS

Series: Applied Mathematics, Mechanics, and Engineering
Vol. 65, Issue Special IV, December, 2022

EXPERIMENTAL RESULTS ON SPECIFIC HEAT CAPACITY OF MWCNT NANOENHANCED PEG FLUID

Elena Ionela CHERECHES, Marius Ionut CHERECHES, Alina Adriana MINEA

Abstract: *The idea of adding nanoparticles to classical heat transfer fluids is a hot research topic, while it is interesting and stimulating, especially through the use of non-conventional fluids, such as polyethylene glycol (PEG). In this research, the specific heat capacity of PEG 400 and MWCNT nanoenhanced PEG 400 fluids was experimentally studied at ambient temperature and with temperature variation in the range of 293.15 and 333.15 K. The specific heat capacity of the samples increased with the temperature and the addition of MWCNT nanoparticles definitely influences this property. The experimental results were also compared with theoretical correlations. In conclusion, the studies on these new fluids are still in their pioneering zone and the experimental effort needs to be intensified.*

Key words: PEG 400, specific heat capacity, nanofluids, MWCNT, nanoparticles.

1. INTRODUCTION

The nanofluid (NF) is made up of a liquid called the base fluid and a solid phase, composed of nano-sized particles. Water, oils and ethylene glycol are most often used as the base fluid, while the nanoparticles (NPs) are divided into three large categories, without excluding other types of NPs studied in detail: metal, oxide and carbon nanotubes. In the present study, the basic fluid used is polyethylene glycol (PEG) 400 and the NPs are MWCNT (multi-walled carbon nanotubes). The special properties of NFs are due to some particularities related to the sizes of suspended particles and thus the research carried out so far in the field of NF has demonstrated their noticeably superior thermal performance compared to any other classical fluids, [1-9].

Specific heat is less studied by the research groups involved in the design of new heat transfer fluids, as was underlined by Minea [4] in a recent paper. In the next few lines several state of the art results will be discussed in terms of NPs types, base fluids and experimental outcomes on specific heat. Chereches et al. [1] studied PEG 400 and prepared NFs with mass concentrations of 0.50, 1.00, 2.50 and 5.00 wt % ZnO NPs, measuring their specific heat at different temperatures. An increase in specific

heat of approximately 5.4% was observed for the NF with a maximum concentration of 5.00% wt compared to the base fluid.

In their manuscript, Marcos et al. [2] measured the specific heat of PEG 400 based on Ag, at temperature varying from room temperature up to 333.15 K. The results indicated that the NPs addition have a very low influence on the specific heat values. Chereches et al. [3] obtained new dispersion of alumina in PEG 400. The specific heat was measured, at different temperatures, depending on the mass concentration of Al₂O₃ NPs (0.25 – 5.00% wt). The results show a slight increase in specific heat with increasing temperature for all studied fluids, so authors conclusion was that the influence of temperature on this property is limited for this particular suspensions.

Another study that used MWCNTs to fabricate NFs was performed by Esfe et al. [5]. They studied another very important thermophysical property for NFs (thermal conductivity) for six fluids based on ethylene glycol, with a volume concentration of MWCNT between 0.02% and 0.75%. For the NF with the highest volume concentration, at a temperature of 323.15 K, the thermal conductivity increased by approximately 45%. Asadi et al. [6] used MWCNTs to make NFs and analyzed their

stability. Their conclusion was that the visual observation method is not reliable for dark colored NFs. Since MWCNTs have a particularly high thermal conductivity of about 2000-3000 W/(m·K) compared to other NPs such as CuO, TiO₂, Al₂O₃ and ZnO, most researchers have studied this property, [7-9], in the detriment of other properties, such as specific heat. Other authors, [10,11] studied the viscosity of some MWCNT/SiO₂ -oil NFs, the studied samples showing a Newtonian behavior.

Currently, the number of publications appearing in the field of new heat transfer fluids (nanofluids) is increasing due to the benefits of introducing new fluids in energy systems. This work can help to define the heat transfer behavior for nanoparticle-enhanced PEG 400, because PEG, as a base fluid for heat transfer, has been relatively slight studied and there are only a few dedicated papers [1-4]. In addition, research in this field is interesting and stimulating, especially through the use of non-conventional fluids, such as PEG.

Thus, there is very little and scattered data regarding the specific heat of NFs based on MWCNT/PEG 400. In this paper was discussed the experimental specific heat of five NFs, with mass concentration of 0.025, 0.050, 0.075, 0.10, 0.50 by dispersing MWCNT in PEG 400.

2. MODELS FOR SPECIFIC HEAT ESTIMATION

Specific heat is one of the relevant properties when heat transfer of fluids is discussed. Usually, specific heat is experimentally determined by DSC measurements. Nevertheless, there are several estimations of nanofluids specific heat that are widely accepted in the open literature dedicated to these new fluids. Furthermore, the theoretical correlations will be depicted, together with some observations. One of the most used estimation for specific heat is defined by a fundamental relationship proposed and validated by Pak and Cho [12]

$$C_{p_{nf}} = \phi(C_p)_p + (1 - \phi)(C_p)_{bf} \quad (1)$$

Equation (1) is one of the first of its kind and was demonstrated to give relatively good results.

Nevertheless, nowadays it was found that a better estimation of experimental results can be achieved with the equation proposed by Xuan and Roetzel [13]:

$$C_{p_{nf}} = \frac{(1 - \phi)(\rho C_p)_{bf} + \phi(\rho C_p)_p}{(1 - \phi)\rho_{bf} + \phi\rho_p} \quad (2)$$

Later on, a new form of equation (2) was written as Equation (3):

$$c_{p_{inf}} = \varphi_{wt}(c_p)_p + (1 - \varphi_{wt})(c_p)_{bf} \quad (3)$$

This equation was proposed by Raud et al. [14] and is recently considered the most reliable and manages to describe with a very good precision the behavior of fluids enhanced with NPs. In Table 2, the volume fractions were calculated using the mass fraction:

$$\frac{1}{\phi} = 1 + \frac{\rho_p}{\rho_{bf}} \left(\frac{1 - \varphi_{wt}}{\varphi_{wt}} \right) \quad (4)$$

In the previous equations (1-4), ϕ represents the volume fraction of NPs, φ_{wt} is the mass fraction, c_p is the specific heat and ρ is the density, the index p refers to NPs, bf to the base fluid, and nf refers to NF.

The results obtained with these two equations (1-2) differ by less than 10%. Thus, both equations can be used for the correct determination of the specific heat of NFs. Similar to density, specific heat depends only on the physical properties of the base fluid and the concentration of solid particles. Moreover, these two properties of NFs, due to the lack of experimental data regarding their temperature dependence, are considered linear functions depending only on the volume fraction. From an experimental point of view, the existing results in specialized literature are extremely deficient.

3. EXPERIMENTAL

The experimental part was conducted both at ambient temperature and when temperature is increasing up to 60 °C. Also, few models of specific heat estimation will be discussed. The PEG 400 (Kollisolv PEG E 400, CAS Number 25322-68-3) with 99.5% purity purchased from Merck (Darmstadt, Germany), was used in this study. Also, Merck (Darmstadt, Germany),

supplied MWCNT NPs with a 50-90 nm reported average size and 95% purity.

Table 1 summarizes the main properties of the materials used in this paper. To obtain the new fluids, was calculated the amount of MWCNT and weighed with a digital balance (Model Sartorius CPA 225 D (Gottingen, Germany). An ultrasonic bath (Model BRANSONIC Model B200), with a frequency of 60 Hz for 60 min was used for dispersing the NPs in base fluid (see more details in Chereches et al. [15]). The NFs obtained, the assigned codes and their composition are mentioned in table 2

Table 1
Chemical properties of the NPs and the base fluid, provided by the manufacturer.

Chemical formula	MWCNT	C ₂ H ₄ O
CAS number	308068-56-6	25322-68-3
Purity	95%	99.5%
Dimension	50-90 nm in diameter, up to 20 μm in length	-
Melting point	3.652 - 3.697 °C	> 300 °C
Molecular mass	-	380 – 420 g/mol
Density	2.3 g/cm ³ at 25 °C	1.125 g/cm ³ at 25 °C [2]
Specific heat	0.711 KJ/Kg °C at 25 °C 0.7333 KJ/Kg °C at 45 °C	2.298 J/Kg·K at 25 °C [1,3]
pH	-	4.5 – 7.0 (50 g/L)
Specific surface area	28 m ² /g (prin adsorbție N ₂)	-
Decomposition temperature	-	> 300 °C
Vapor pressure	-	< 0.01 hPa at 20 °C

The analysis of the specific heat of the NFs was carried out with a DSC 1 equipment from Mettler Toledo, equipped with a dedicated STAR software. As a description, the tests were performed in the same initial conditions using hermetic aluminum capsules (40 μL). All the samples were weighted before the test and the results revealed a mass between 6 and 11 mg, depending on each sample. In addition, several cycles of heating – cooling were considered and the samples are cooled by means of the IntraCooler system, that is part of the equipment. The temperature ranges for which the specific

heat was measured was between 283.15 - 333.15 K, and 3-5 tests were performed for each sample, the final value being the arithmetic mean of the individual values for each test.

Table 2
Manufactured fluids and their code.

Code	Mass fraction of NPs, -	Volume fraction of NPs, -	Density, Kg/cm ³
PEG 400	0.00000	0.00000	1125.00
PEG 400 + 0.025% MWCT	0.00025	0.00013	1125.13
PEG 400 + 0.050% MWCT	0.00050	0.00027	1125.26
PEG 400 + 0.075% MWCT	0.00075	0.00040	1125.39
PEG 400 + 0.10% MWCT	0.0010	0.00054	1125.52
PEG 400 + 0.50% MWCT	0.0050	0.00268	1127.62

4. RESULTS AND DISCUSSIONS

The specific heat of the NFs was calculated using the data provided by DSC, namely, the heat flux, the thermal gradient and the mass of the sample, while the results are presented in figure 1 and 2. The relative specific heat depicted in figure 2 was calculated as the ratio between the specific heat of the NFs and that of the base fluid.

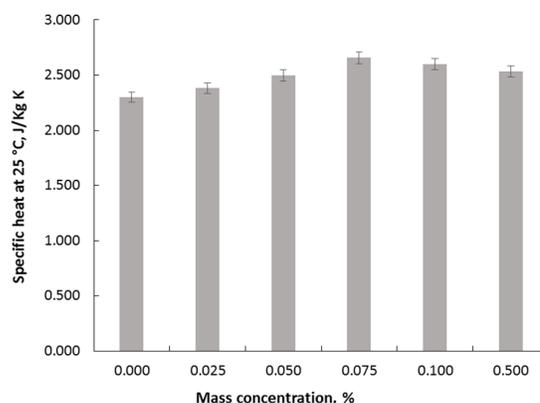


Fig. 1. Specific heat depending on the mass concentration of the NPs, at a temperature of 25 °C.

Figure 1 shows the variation of the specific heat depending on the mass concentration of NPs at a temperature of 25 °C for the five studied fluids, the mass concentrations being in the range of 0.025 - 0.500% wt. It can be seen that the specific heat increases with the addition of NPs up to 0.075, the increase being 6%, then

decreases. This phenomenon was also noticed in the specialized literature, [3] where a slight increase in the specific heat (approximately 5%) was observed with the increase in the concentration of Al₂O₃ NPs. But the results published by Chereches et al [1] for PEG 400 – ZnO NFs, do not agree with these data, so it is obvious that specific heat is influenced by the type of nanoparticle, as well as the base fluid type.

Figure 2 presents the variation with temperature of the specific heat and it can notice that the specific heat increases with increasing temperature, which is a general phenomenon valid for the vast majority of liquids. The outcomes from figure 2 clearly indicate an increase in relative specific heat with temperature, the largest increase being observed for the NF with 0.075 wt % MWCNT. In the case of the PEG 400 base fluid, the increase in specific heat with temperature is very small, almost insignificant. The data reported here for PEG-400-MWCNTs do not agree with the results obtained by Marcos et al. [16], mainly because in this case the specific heat for pure PEG 400 is lower than that of NFs.

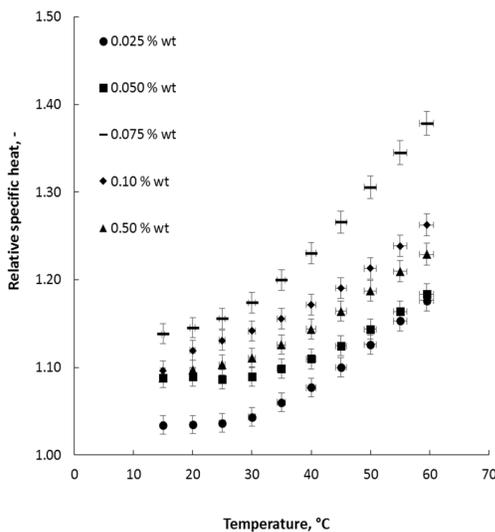


Fig. 2. Variation of relative specific heat with temperature.

Figure 3 shows a comparison of the specific heat with the two theoretical models discussed in the previous section. As can be seen from figure 3, for small concentrations of NPs the differences are extremely small, and it can see

that the specific heat decreases with the upsurge in concentration of NPs.

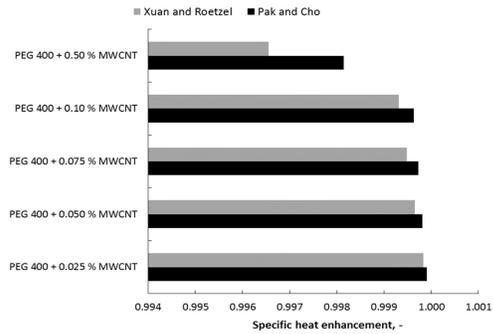


Fig. 3. Specific heat comparison between two theoretical models.

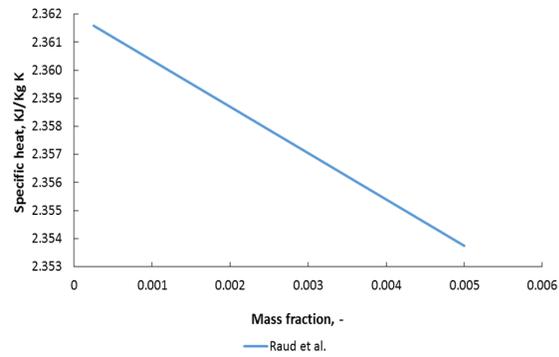


Fig. 4. Variation of the theoretical specific heat.

The variation of the specific heat according to the mass fraction, calculated with the equation of Raud et al. is presented in figure 4, where it can notice that the specific heat decreases linearly with the increase in the concentration of NPs.

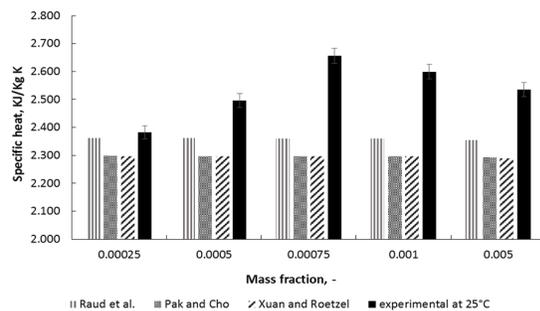


Fig. 5. Comparison between experimental and theoretical data.

Figure 5 shows a comparison between the experimental data at the ambient temperature (i.e., 25 °C) and the three theoretical models. As can be seen from figure 5, these models are not able to correctly estimate the experimental values of the specific heat for these particular

PEG based fluids. Besides, Pak and Cho and Xuan and Roetzel models give similar results, the differences being less than 10%, and the three models do not show variations in specific heat with increasing mass fraction, compared to the experimental data where a clear difference is observed with the addition of NPs.

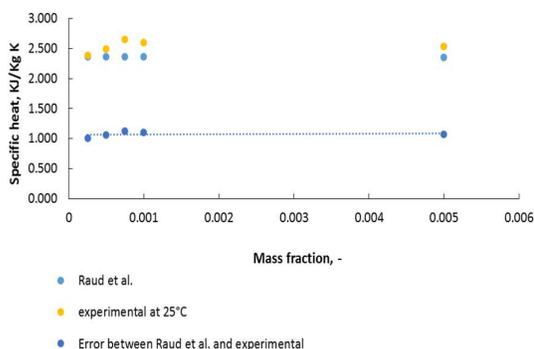


Fig. 6. Comparison between experimental and Raud et al. [14].

The data presented in figure 6 show an error of approximately 1.2% of the theoretical specific heat calculated with the equation of Raud et al., compared to the experimental data. In conclusion, it could be said that the equation of Raud et al. [14] is the most appropriate equation to describe the experimental values for the studied NFs.

5. CONCLUSION

In conclusion, it can say that the specific heat of the studied NFs is strongly influenced by both the addition of NPs to the base fluid and the temperature. The comparison of the experimental data with the theoretical equations revealed that no theoretical model is able to estimate the increase in specific heat when solid NPs are added to the PEG base fluid. Plus, the experimental results revealed that the specific heat increases with the addition of NPs up to 0.075 wt %, then decreases and increases with temperature, while for the base fluid the increase is very small, almost insignificant. As a general conclusion, PEG 400 shows high potential for use in a series of practical applications; however, additional studies are needed in regard to this class of NFs.

6. ACKNOWLEDGMENTS

This paper was supported by a grant of the Romanian Ministry of Education and Research, CNCS-UEFISCDI, project number PD 36/2022, code project PN-III-P1-1.1 - PD-2021-0222, within PNCIDI III.

7. REFERENCES

- [1] Chereches, M., Bejan, D., Ibanescu, C., Danu, M., Chereches, E.I., Minea, A.A. *Viscosity and isobaric heat capacity of PEG 400-Based Phase Change Materials Nano-Enhanced with ZnO nanoparticles*. J Therm Anal Calorim, 147, 8815–26, 2022, <https://doi.org/10.1007/s10973-021-11171-w>
- [2] Marcos, M.A., Cabaleiro, D., Guimarey, M.J.G., Comuñas, M.J.P., Fedele, L., Fernández, J., Lugo, L. *PEG 400-based phase change materials nano-enhanced with functionalized graphene nanoplatelets*, Nanomaterials, 8(16), 2018, <https://doi.org/10.3390/nano8010016>
- [3] Chereches, M., Ibanescu, C., Danu, M., Chereches, E.I., Minea, A.A. *PEG 400-Based Phase Change Materials Nano-Enhanced with Alumina: an experimental approach*. Alex Eng J, 6(9), 6819-30, 2022, <https://doi.org/10.1016/j.aej.2021.12.029>
- [4] Minea, A.A. *State of the Art in PEG-Based Heat Transfer Fluids and Their Suspensions with Nanoparticles*. Nanomaterials, 11(1), 86, 2021, <https://doi.org/10.3390/nano11010086>
- [5] Esfe, M.H., Firouzi, M., Afrand, M. *Experimental and theoretical investigation of thermal conductivity of ethylene glycol containing functionalized single walled carbon nanotubes*. Physica E, 95, 71–7, 2018, <https://doi.org/10.1016/j.physe.2017.08.017>
- [6] Asadi, A., Asadi, M., Rezaniakolaei, A., Rosendahl, L.A., Wongwises, S. *An experimental and theoretical investigation on heat transfer capability of Mg (OH) 2/MWCNT-engine oil hybrid nano-lubricant adopted as a coolant and lubricant fluid*. Appl Therm Eng, 129, 577–86, 2018, <https://doi.org/10.1016/j.applthermaleng.2017.10.074>
- [7] Kim, P., Shi L., Majumdar, A., McEuen, P. *Thermal transport measurements of individual multiwalled nanotubes*. Phys Rev Lett, 87,

- 215502, 2001, <https://doi.org/10.1103/PhysRevLett.87.215502>
- [8] Leong, K.Y., Hanafi, N.M., Sohaimi, R.M., Amer, N.H. *The effect of surfactant on stability and thermal conductivity of carbon nanotube based nanofluids*. Therm Sci, 20(2), 429-436, 2016, https://doi.org/10.2298/TSCI13091407_8L
- [9] Sandhu, H.K., Dasaraju, G. *An Experimental Study on Stability and Some Thermophysical Properties of Multiwalled Carbon Nanotubes with Water-Ethylene Glycol Mixtures*. Part Sci Technol, 35(5), 547-54, 2016, <https://doi.org/10.1080/02726351.2016.1180335>
- [10] Hemmat Esfe, M., Afrand, M., Yan, W.-M., Yarmand, H., Toghraie, D., Dahari, M. *Effects of temperature and concentration on rheological behavior of MWCNTs/SiO₂ (20–80)-SAE40 hybrid nano-lubricant*. Int Commun Heat Mass Transf, 76, 133–8, 2016, <https://doi.org/10.1016/j.icheatmasstransfer.2016.05.015>
- [11] Afrand, M., Nazari, Najafabadi, K., Akbari, M. *Effects of temperature and solid volume fraction on viscosity of SiO₂-MWCNTs/SAE40 hybrid nanofluid as a coolant and lubricant in heat engines*. Appl Therm Eng, 102, 45–54, 2016, <https://doi.org/10.1016/j.applthermaleng.2016.04.002>
- [12] Pak, B.C., Cho, Y.I. *Hydrodynamic and heat transfer study of dispersed fluids with submicron metallic oxide particles*. Exp Heat Transf, 11(2), 151–70, 1998, <https://doi.org/10.1080/08916159808946559>
- [13] Xuan, Y., Roetzel, W. *Conceptions for heat transfer correlation of nanofluids*. Int J Heat Mass Transf, 43(19), 3701–7, 2000, [https://doi.org/10.1016/S0017-9310\(99\)00369-5](https://doi.org/10.1016/S0017-9310(99)00369-5)
- [14] Raud, R., Hosterman, B., Diana A., Steinberg T.A., Will G. *Experimental study of the interactivity, specific heat, and latent heat of fusion of water based nanofluids*. Appl Therm Eng, 117, 164–8, 2017, <https://doi.org/10.1016/j.applthermaleng.2017.02.033>
- [15] Chereches, M., Vardaru, A., Huminic, G., Chereches, E.I., Minea, A.A., Huminic, A. *Thermal conductivity of stabilized PEG 400 based nanofluids: An experimental approach*. Int Commun Heat Mass Transf, 130, 105798, 2022, <https://doi.org/10.1016/j.icheatmasstransfer.2021.105798>
- [16] Marcos, A.M., Podolsky, E.N., Cabaleiro, D., Lugo, L., Zakharov, O.A., Postnov, N.V., Charykov, A.N., Ageev, V.S., Semenov, N.K. *MWCNT in PEG-400 nanofluids for thermal applications: A chemical, physical and thermal approach*. J Mol Liq, 294, 111616, 2019, <https://doi.org/10.1016/j.molliq.2019.111616>

REZULTATE EXPERIMENTALE PRIVIND CĂLDURA SPECIFICĂ A FLUIDULUI PEG NANO-ÎMBUNĂTĂȚIT CU MWCNT

Ideea de a adăuga nanoparticule în fluidele clasice de transfer de căldură este un subiect de cercetare interesant și de actualitate, în special prin utilizarea fluidelor neconvenționale, cum ar fi polietilenglicolul (PEG). În această lucrare, căldura specifică a fluidelor PEG 400 nano-îmbunătățite cu MWCNT a fost studiată experimental la temperatură ambiantă și la variația cu temperatură în intervalul 293,15 și 333,15 K. Căldura specifică a nanofluidelor a crescut odată cu temperatura și adăugarea nanoparticulelor de MWCNT. În plus, datele experimentale au fost comparate cu modelele teoretice existente. În concluzie, studiile asupra acestor noi fluide sunt încă în zona lor de pionierat și efortul experimental trebuie intensificat.

Elena Ionela CHERECHES, dr.eng., assistant, Technical University “Gheorghe Asachi” of Iasi, Department of Materials Science, elena-ionela.chereches@academic.tuiasi.ro.

Marius Ionut CHERECHES, PhD, student, Technical University “Gheorghe Asachi” of Iasi, Department of Technologies and Equipment for Materials Processing, marius-ionut.chereches@student.tuiasi.ro.

Alina Adriana MINEA, prof.dr.eng., professor, Technical University “Gheorghe Asachi” of Iasi, Department of Technologies and Equipment for Materials Processing, alina-adriana.minea@academic.tuiasi.ro.