Nanofluids: Why we love them?

Divna M. Majstorović and Emila M. Živković

University of Belgrade, Faculty of Technology and Metallurgy, Belgrade, Serbia

Abstract

The rising need for fluids with significantly improved heat transfer properties led to the development of nanofluids. The first experiments showed encouraging results reflected in increased thermal conductivity and heat transfer coefficient accompanied with better stability than colloid suspension. Many research laboratories and companies observed the potential of nanofluid technology for specific industrial applications. However, after publication of numerous papers with contradictory results for the same or similar nanofluids, many issues arose. Although in some branches of industry nanofluids have already found practical applications, at some point researchers went back to basics, conducting extended studies and benchmark tests in attempt to explain the nanoparticle influence on thermophysical properties of nanofluids. The final goal of the whole scientific community is to produce nanofluids at low cost, exhibiting long-term stability, and good fluidity as the three most significant preconditions toward practical applications in the heat transport field.

Keywords: Thermophysical properties; thermal conductivity; dispersion stability.

Available on-line at the Journal web address: http://www.ache.org.rs/HI/

TECHNICAL PAPER

UDC: 544.773.42-022.513.2

Hem. Ind. **78(2)** 105-111 (2024)

1. INTRODUCTION

The term “nanofluid” was presented to the scientific community in the 90s, while the expansion of research involving nanofluids started a few years later and never stopped. According to the Web of Science, this topic followed the exponential growth in the number of publications per year: from only 4 in the 2020, to more than 1400 papers 15 years later and up to 5000 papers in 2022. It is estimated that more than 300 research groups in academic institutions and companies are involved in nanofluid research worldwide, covering all topics from basic research to high-tech applications.

What lies behind the popularity of nanofluids? Are they really that superior to conventional fluids? Or is it simply the fact that it pays to think "nano" regardless of whether you are applying for research funding or marketing a new product? Before answering these questions, let's briefly recall what nanofluids really are and what we can achieve with them.

This new class of fluids contains particles in the size range under 100 nm which are uniformly and stably suspended in a liquid. Adding the nanoparticles to the base fluid will lead to changed effective thermophysical properties. The term effective means that the base fluid is not affected itself, but a new type of fluid is created, consisting of the base fluid and nanoparticles dispersed in it. Dilute colloidal dispersions of nanosized particles in a fluid have exhibited some advantageous features compared to larger particles suspended in a liquid, such as improved heat transfer, longer shelf life, and control of suspension stability. Also, as a result of the small size of nanoparticles, channel clogging and erosion of walls are less pronounced as compared to the use of larger particles, which is a unique combination of features most highly desired for different engineering applications.

Nanofluids can significantly improve/change properties of the base fluid such as thermal conductivity, specific heat, heat transfer coefficient, absorption, refractive index, lubricity, electric conductivity, etc. The much larger surface area of nanoparticles relative to those of conventional particles should not only improve heat transfer capabilities, but also increase the stability of suspensions. Due to the large area of potential usage, the most investigated nanoparticles include metals and oxides, but also carbides, nitrides or carbon tubes, while base fluids are usually water, ethylene glycol, oils or ionic liquids.

Corresponding authors: Divna M. Majstorović, University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, 11120 Belgrade, Serbia Paper received: 8 November 2023; Paper accepted: 12 June 2024; Paper published: 28 June 2024.
E-mail: sdbajic@tmf.bg.ac.rs
https://doi.org/10.2298/HEMIND231108011M

2. NANOFLUID PREPARATION AND STABILITY

Over the years the preparation methods of nanofluids also experienced some changes. Firstly, researchers generated nanoparticles directly in the base fluids without the need for a redispersion process, but nowadays as nanoparticles are widely commercially available, preparation of nanofluids follows the so-called two step method. In the first step, nanoparticles are produced or bought and then, in the second, dispersed in the base fluid at the desired concentration.

But, although the two-step method seems "easier", researchers report that stability is a significant issue in this method as nanopowders aggregate easily because of the strong van der Waals force among nanoparticles. The one-step method seems to produce more stable nanofluids [1]. Another advantage of the one-step method is that drying, storage, transportation, and nanoparticle dispersion are avoided. The main fault of this method is that residual reactants remain in the nanofluids because of incomplete reaction or stabilization. Also, synthesizing nanofluids on a large scale is difficult when employing the one-step method. Thus, the two-step method is the most economical method for large-scale production of nanofluids because nanopowder synthesis techniques have already been scaled up to industrial production levels. For dispersion of nanoparticles in the base fluid different dispersion methods can be used to gain the stability of nanofluids such as sonication, homogenization and ball milling.

Figure 1 presents a stable nanofluid with uniformly dispersed nanoparticles in the base fluid on the left side, and an unstable nanofluid with nanoparticles quickly settling down after preparation, on the right side.

Figure 1. Photographs of a stable (a) and an unstable (b) nanofluid

Stabilization depends upon the choice of nanoparticles and a proper dispersion method. Hence, preparation and stabilization of nanofluids sets an exciting challenge to a researcher since the main objective and goal in nanofluid research is to develop a nanofluid with adequate stability for industrial applications. Along with the visual test to monitor agglomeration and sedimentation over time, UV-Vis spectroscopy and zeta potential measurements were adopted to observe stability of nanofluids. Other techniques include dynamic light scattering and laser diffraction analysis for particle size investigations.

How much only sonication mode, continuous or discontinues pulses used in nanofluid preparation, can influence the particle distribution and stability of the prepared nanofluid can be seen in [2]. It is shown that discontinuous vibrations cannot break the clusters and provide good distribution of nanoparticles and achieve constant stability of a nanofluid over long period of time.

Another aspect regarding stability of nanofluids that has to be considered is the usage of surfactants or dispersants, which, on the other hand, may affect the properties of nanofluids [3]. This information is often either intentionally or inadvertently neglected, which leads to apparently different experimental results for nominally the same fluids. Few papers over the years were dealing with this issue and concluded that addition of a surfactant remarkably affects transport properties and heat transfer performance of nanofluids and may be responsible for the discrepancy among the experimental data obtained for nanofluids in different research groups. Although their usage can help to enhance nanoparticle stability in fluids, the functionality of surfactants for high-temperature applications of nanofluids is a major concern.

3. THERMOPHYSICAL PROPERTIES OF NANOFLUIDS

Basic research of nanofluids is usually focused on the effect that nanoparticles have on thermophysical properties of the base fluid. Despite the attention this field has received in recent years, uncertainties concerning the fundamental effects of nanoparticles on these properties of solvent media remain [4]. Four thermophysical properties, *i.e.* density, specific heat, thermal conductivity, and viscosity, are intensely discussed in the literature, among which thermal conductivity is the property that has catalysed attention of the nanofluids research community the most. Based on experimental measurements, it was determined that the increase in thermal conductivity is mostly influenced by the concentration and shape of particles, as well as temperature and pressure in the system. It is interesting that the increase is often greater than the value which could be predicted by conventional theories. Several attempts were made to incorporate these results into correlations.

Due to large discrepancies and inconsistencies regarding the degree of thermal conductivity enhancement of the "same" nanofluids, a comprehensive International Nanofluid Property Benchmark Exercise was conducted [5]. Thirty-four organizations worldwide received identical samples of nanofluids in order to measure thermal conductivity using different experimental methods (the transient hot wire method, steady-state and optical methods). Four sets of test samples were procured covering variety of base fluid and different nanoparticles material, shape and concentration.

Three main conclusions were established: (i) the thermal conductivity enhancement rises with increasing the particle concentration and decreasing the base fluid thermal conductivity, (ii) deviations between experimental data obtained by different labs for the same samples fall within 10 %, which is attributed to the different measurement methods, and (iii) any anomalous enhancement of thermal conductivity was not observed and the classic theory accurately described the behaviour of thermal conductivity of nanofluids. Although some deviations are noticeable for directly measured thermal conductivities, the calculated enhancement of this parameter showed much better agreement between different labs since the same measurement technique at the same temperature conditions was also used to measure the thermal conductivity of the base fluid.

Figure 2 presents one of the graphs for the experimental thermal conductivity data of Au + water nanofluid sample [5]. There are noticeable deviations in the graph between the values obtained by different measurement methods at different laboratories as well as somewhat higher reported uncertainties for some of the results.

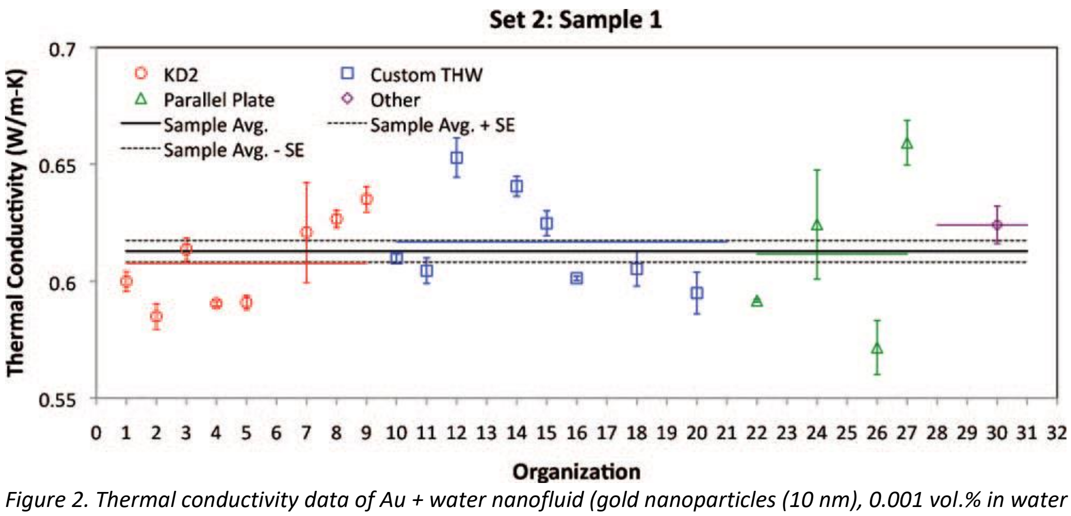

Figure 2. Thermal conductivity data of Au + water nanofluid (gold nanoparticles (10 nm), 0.001 vol.% in water + stabilizer) at room temperature, measured by different organizations and measurement methods: the KD2 Decagon thermal properties analyser, custom thermal hot wire (THW), steady state parallel plate and other techniques. The solid line represents the average of all data points, and the dotted lines are the standard error of the mean. Reprinted from Buongiorno et al. [5], with permission. Copyright [2009] by the AIP Publishing

From all mentioned above, it can be summarized that the complicated enhancement mechanism in nanofluids originate from several factors such as the physical properties of nanoparticles and base liquids, size and shape distribution of nanoparticles, volume fraction and agglomeration of suspended nanoparticles and the interaction between nanoparticles and the base fluid.

An interesting type of a nanosuspension should be mentioned which were obtained by suspending particles generated from biomass in a base fluid. The aim of these studies was to develop biofluids that would be an alternative to existing nanofluids. Queirós et al [6] investigated ionic biofluids as dispersions of ground lignocellulosic biomass in the mixture of 1-ethyl-3-methylimidazolium acetate [EMIM][OAc] with water as a base fluid. In this way, the researchers actually obtained a microfluid with a size of suspended particles smaller than 180 µm. With a small amount of suspended particles (1 wt.%), thermal conductivity of the base fluid did not increase. However, a significant increase in this parameter of 35 % was achieved at a mass concentration of particles of 3 wt.% at room conditions. Radojčin *et al.* [7] produced particles from sunflower stalks using hydrothermal carbonization and heat treatment in an inert atmosphere oven. The fraction of fine particles with mean peak diameter of 729.5 nm was about 20 %. The generated particles were suspended in the ionic liquid 1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl)imide [HMIM][NTf_2] as a base fluid. The thermal conductivity of the dispersion increased by ~12 % relative to the ionic liquid in the case of 5 wt.% mass concentration of particles. The study was repeated with ethylene glycol as a base fluid and the thermal conductivity of the dispersion increased by 10 % relative to ethylene glycol in the case of 5 wt.% mass concentration of particles [8].

4. PRACTICAL APLICATIONS OF NANOFLUIDS

Applied research on nanofluids is focused on various fields: electronics, transportation, medicine, solar cells, sensors, cooling, micro-electromechanical systems (MEMS), tuneable optical fibres, optical switches, *etc*. Nanofluids are mentioned mainly as cooling agents in the automotive sector, fuel cells, electronics, in refrigeration or heat pump cycles and as a phase change material [4]. A great area of potential usage of nanofluids is for solar thermal absorbers where numerous publications can be found, but little experience exists regarding pilot scale or full-scale plants. Information about high temperature, high pressure and long-term behaviour of nanofluids in mentioned systems is lacking. Therefore, besides basic research it is of great importance to expand studies to specific applications, realized in a suitable environment. Figure 3 provides a scheme for practical applications of nanofluids.

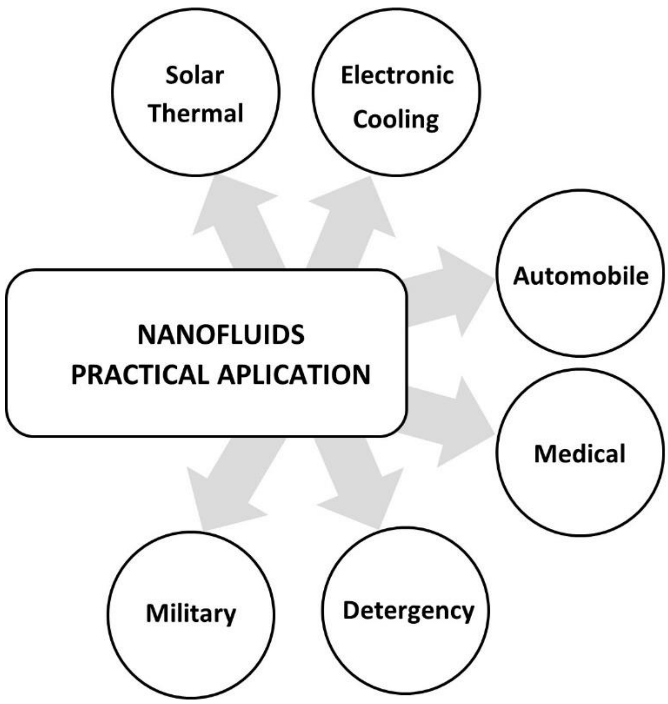

Figure 3. Schematic presentation of possibilities for practical applications of nanofluids

Given that the highest influence of nanoparticles is exerted on the thermal conductivity of the base fluid, it is inevitable that a large number of papers dealing with the practical application of nanofluids are focused on heat exchangers.

In order to validate a nanofluid as a heat transfer fluid, forced convection in nanofluids is often investigated. The concept of convective heat transfer of nanofluids through a straight pipe section is mostly studied by analysing the Nusselt number and convective heat transfer coefficient [9]. Yet, still high costs of nanofluids pose a problem in conducting such experimental research. As a result, small-volume facilities have to be used for testing the forced convection of nanofluids, which is a real challenge from the point of view of development and performance of such facilities [10,11]. This is the reason why computational fluid dynamics (CFD) is widely used for the purposes of research of forced convection of nanofluids [12-14].

The experimental data showed that, among other factors, the flow regime within this equipment is essential for the effectiveness of a nananofluid. Under laminar flow conditions the heat exchanger operates at high costs and the nanofluid stability cannot be guaranteed. On the other hand, using nanofluids when a heat exchanger operates under turbulent flow conditions is beneficial only if the increase in thermal conductivity is accompanied by a marginal increase in viscosity, which is very difficult to achieve [4].

A class of nanofluids that is singled out due to the influence of its magnetic effect on heat transfer is also tested for usage in heat exchangers as a heat transfer fluid. These magnetic nanofluids, also called the ferrofluids, contain the single-domain superparamagnetic materials (ferro or ferromagnetic) in the size range of 3-15 nm coated with a surfactant or polymer, and dispersed in the base fluid [15]. Particles commonly used are metals (iron, cobalt, nickel etc.) or metal oxides, while dispersion mediums include polar solvents (water and ethylene glycol) and non-polar solvents like kerosene, silicone oil, mineral oil, *etc*. Most of the experimental research refers to Fe_3O_4 - water nanofluids with applying the external constant and alternating magnetic field under the laminar forced convective heat transfer in the tube. Published studies showed that the convective heat transfer is increased with the increase in the magnetic field strength and nanoparticle concentration, in the heat exchangers operating at low and moderate Reynolds numbers. Depending on the investigated magnetic intensities, particle concentrations and flow conditions the heat transfer coefficient of a ferronanofluid increases by approximately 13 to 75 % when using a magnetic force as compared to the one without a magnetic force, as summarized by Narankhishig *et al.* [16].

Of course, many challenges have to be faced before the practical application of nanofluids. After determining the impact of nanoparticles, especially their shape, size, type, concentration, and dispersion on the base fluid as well as the need for a surfactant to improve the nanofluid stability, still several issues arise before practical implementation. Some of these are conditions under which the nanofluid will be used, its behaviour during some extended periods, its scale-up capacity and inevitable increase in viscosity. Viscosity is important in designing nanofluids for flow and heat transfer applications because the pressure drop, and the resulting pumping power depend on this parameter. Another issue, sometimes even more important, is the cost of designing nanofluids and accompanying costs of introducing this new class of fluids in everyday use.

One more aspect that needs to be addressed and relates to non-engineering applications is the influence of nanofluids on the human health. Although nanofluids already found applications in medicine and cosmetic industry (nanodrug delivery, cancer therapy, sunscreens, *etc*.), tolerability and safety for human body during use of numerous products (textiles to cosmetics) have to be further investigated for possible long-term effects.

4. CONCLUSION

Although a lot has been done in the field of nanofluid research, there is still a lot of work ahead of us. The search for efficient methods of producing stable nanofluids on a large scale is still ongoing. Investigation of thermophysical properties of nanofluids requires more effort. To deduce adequate equations for a wide range of conditions, more and better coordinated basic research is needed. At present, experimental data and measurement methods and techniques are lacking consistency.

Having all this in mind let's try to answer the questions from the beginning of the text: Is it just a matter of fashion or something more is hidden behind the popularity of nanofluids? The most honest answer would be: Yes, it seems that nanofluids really have the potential for significant practical applications, but we are still far from fully exploiting it.

Acknowledgements: The authors gratefully acknowledge the financial support received from the Research Fund of Ministry of Science, Technological Development and Innovation of the Republic of Serbia and the Faculty of Technology and Metallurgy University of Belgrade (Contract No. 451-03-47/2023-01/200135).

REFERENCES

[1] Solangia KH, Kazia SN, Luhurb MR, Badarudina A, Amiria Rad Sadria A, Zubira Samira Gharehkhania MNM, Teng KH. A comprehensive review of thermo-physical properties and convective heat transfer to nanofluids. *Energy* 2015; 89: 1065-1086 https://doi.org/10.1016/j.energy.2015.06.105.

[2] Tajik B, Abbassi A, Saffar-Avval M, Ahmadi Najafabadi M. Ultrasonic properties of suspensions of TiO_2 and Al_2O_3 nanoparticles in water. *Powder Technol.* 2012; 217: 171-176 https://doi.org/10.1016/j.powtec.2011.10.024.

[3] Xuan Y, Li Q, Tie P. The effect of surfactants on heat transfer feature of nanofluids. *Exp Therm Fluid Sci.* 2013; 46: 259-262 https://doi.org/10.1016/j.expthermflusci.2012.12.004.

[4] Eggers JR, Kabelac S. Nanofluids revisited. *Appl Therm Eng.* 2016; 106: 1114-1126 https://doi.org/10.1016/j.applthermaleng.2016.06.100.

[5] Buongiorno J, Venerus DC, Prabhat N, McKrell T, Townsend J, Christianson R, Tolmachev YV, Keblinski P, Hu L, Alvarado JL, Bang IC, Bishnoi SW, Bonetti M, Botz F, Cecere A, Chang Y, Chen G, Chen H, Chung SJ, Chyu MK, Das SK, Di Paola R, Ding Y, Dubois F, Dzido G, Eapen J, Escher W, Funfschilling D, Galand Q, Gao J, Gharagozloo PE, Goodson KE, Gutierrez JG, Hong H, Horton M, Hwang KS, Iorio CS, Jang SP, Jarzebski AB, Jiang Y, Jin L, Kabelac S, Kamath A, Kedzierski MA, Kieng LG, Kim C, Kim J-H, Kim S, Lee SH, Leong KC, Manna I, Michel B, Ni R, Patel HE, Philip J, Poulikakos D, Reynaud C, Savino R, Singh PK, Song P, Sundararajan T, Timofeeva E, Tritcak T, Turanov AN, Van Vaerenbergh S, Wen D, Witharana S, Yang C, Yeh W-H, Zhao X-Z, Zhou S-Q. A benchmark study on the thermal conductivity of nanofluids. *J Appl Phys.* 2009; 106: 094312 http://dx.doi.org/10.1063/1.3245330.

[6] Queirós CSGP, Lourenço MJV, Santos FJV, Nieto de Castro CA. IoBiofluids: A sustainable alternative to current heat transfer fluids. In: *Proceedings of the 2nd European symposium on nanofluids (ESNf2019).* Castelló, Spain, 2019, pp. 452-455.

[7] Radojčin M, Bikić S, Pavkov I, Bukurov M, Despotović B, Stamenković Z, Oluški N. Experimental investigation on thermophysical properties of iobiofluids. *Adv Mech Eng.* 2022; 14 https://doi.org/10.1177/16878140221075457.

[8] Bikić S, Radojčin M, Pavkov I, Bukurov M, Despotović B, Stamenković Z, Oluški N, Al Afif R. Thermophysical dispersion properties of agricultural biomass particles in ethylene glycol. *Int J Thermofluids* 2022; 16: 100226 https://doi.org/10.1016/j.ijft.2022.100226.

[9] Ding Y, Wen D. Experimental investigation into convective heat transfer of nanofluids at the entrance region under laminar flow conditions. *Int J Heat Mass Tran.* 2004; 47: 5181-5188 https://doi.org/10.1016/j.ijheatmasstransfer.2004.07.012.

[10] Laloš S, Bukurov M, Vraneš M, Papović S, Knežević D, Bikić S. The Laboratory Facility for the Research of Forced Convection of Nanofluids - Verification of Hydraulic Parameters. In: *Proceedings of the 10th International Scientific and Expert Conference (TEAM2022).* Slavonski Brod, Croatia, 2022, pp. 185-193.

[11] Laloš S, Bukurov M, Vraneš M, Papović S, Knežević D, Bikić S. Validation of the Laboratory Facility for the Nanofluids Forced Convection Research. In: Karakoc TH, Kostić IA, Grbović A, Svorcan J, Dalkiran A, Ercan AH, Peković OM, eds. *Novel Techniques in Maintenance, Repair, and Overhaul. Proceedings of the International Symposium on Aviation Technology, MRO, and Operations 2022. Sustainable Aviation.* Switzerland: Springer Cham; 2023:377-383 https://doi.org/10.1007/978-3-031-42041-2_48.

[12] Berberović E, Bikić S. Computational Study of Flow and Heat Transfer Characteristics of EG-Si_3N_4 Nanofluid in Laminar Flow in a Pipe in Forced Convection Regime. *Energies* 2020; 13: 74 https://doi.org/10.3390/en13010074.

[13] Hasečić A, Almutairi JH, Bikić S, Džaferović E. Numerical Analysis of Heat Transfer Performances of Ionic Liquid and Ionanofluids with Temperature-Dependent Thermophysical Properties. *Energies* 2021; 14: 8420 https://doi.org/10.3390/en14248420.

[14] Hadžić A, Hasečić A, Bikić S, Džaferović E. Numerical Modeling of Forced Convection of Ionic Liquid [C_4mpyrr][NTf_2], *AIP Conf. Proc.* 2022; 2425: 420024 https://doi.org/10.1063/5.0081414.

[15] Philip J. Magnetic nanofluids (Ferrofluids): Recent advances, applications, challenges, and future directions. *Adv Colloid Interfac.* 2023; 311: 102810 https://doi.org/10.1016/j.cis.2022.102810.

[16] Narankhishig Z, Ham J, Lee H, Cho H. Convective heat transfer characteristics of nanofluids including the magnetic effect on heat transfer enhancement - a review. *Appl Therm Eng.* 2021; 193: 116987 https://doi.org/10.1016/j.applthermaleng.2021.116987.

Nanofluidi: Zašto ih volimo?

Divna M. Majstorović i Emila M. Živković

Univerzitet u Beogradu, Tehnološko-metalurški fakultet, Beograd, Srbija

(Stručni rad)

Izvod

Rastuća potreba za fluidima sa značajno poboljšanim svojstvima za prenos toplote dovela je do razvoja nanofluida. Prvi eksperimenti su pokazali ohrabrujuće rezultate koji se ogledaju u povećanju toplotne provodljivosti i koeficijenta prenosa toplote praćene boljom stabilnošću od koloidne suspenzije. Mnoge istraživačke laboratorije i kompanije uočile su potencijal nanotehnologije za specifične industrijske primene. Međutim, mnoga pitanja su se pojavila nakon objavljivanja brojnih radova sa kontradiktornim rezultatima za iste ili slične nanofluide. Iako su u nekim granama industrije nanofluidi već našli praktičnu primenu, istraživači su se u nekom trenutku vratili osnovama, pokušavajući da objasne uticaj nanočestica na termofizička svojstva nanofluida sprovodeći opširne studije i uporedne testove. Konačni cilj cele naučne zajednice je proizvodnja nanofluida sa dugotrajnom stabilnošću i dobrom fluidnošću, uz niske troškove, kao tri najznačajnija preduslova za praktičnu primenu u oblasti prenosa toplote.

Ključne reči: termofizička svojstva; toplotna provodljivost; stabilnost disperzije