



REGULAR ARTICLE

Effects of Surface Modification, Temperature, and Mass Fraction on Thermal Properties of Nano-graphite/Water Nano-fluid

B. Pratap¹, G. Sahu², S.P. Mahapatra¹

¹ Department of Chemistry, National Institute of Technology, 492010 Raipur, Chhattisgarh, India

² Department of Mechanical Engineering, Government Engineering College, 492015 Raipur, Chhattisgarh, India

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Nano-graphite (NG) and acid modified nano-graphite (ANG) nanoparticles were synthesized from graphite powder using a strong acid i.e. a mixture (sulphuric acid and nitric acid). The optical study and stability of NG and ANG/water nano-fluids were determined by using Ultraviolet-visible spectroscopy measurement. The thermal properties including thermal conductivity, thermal diffusivity and volumetric heat capacity of the nano-fluids were measured in the mass fraction range 0 – 0.053 wt% and at temperature range of 20 – 80°C. The thermal conductivity and thermal diffusivity of the nano-fluids show considerable rise, whereas volumetric heat capacity reduced with NG and ANG concentrations. The thermal conductivity improvement of the nano-fluid shows a considerable rise, with maximal increases of 67.64% and 75.97% for 0.053 wt% NG and ANG loadings, respectively. The volumetric heat capacity of the nano-fluids reductions with rise in mass fraction of NG and ANG and increases with increase in temperature. As a result, ANG nanoparticles are more effective at raising the thermal conductivity of water-based nanofluids, then the NG particles at given the above mass fraction loadings. Finally, based on the findings, in terms of thermal characteristics in practical systems, nano-fluids can be determined to be a viable alternative to water-based fluids.

Keywords: Synthesis, Nano-graphite, Surface modification, Nano-fluids, Thermal properties.

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1. INTRODUCTION

The transfer of heat in any industry is most significant. The demand for new technologies for improving heat transfer is arising due to the fast improvement and expansion of infrastructure in defense, industrial and transportation sectors. The conservative heat transfer technique in industries involves the transportation of heat by a medium like ethylene glycol, water and mineral oil [1, 2]. The use of this type of thermal fluid is needed to improve the heat transfer and support the advancements in the technologies [3]. In 1995 the Choi and Eastman [4] introduced nano-fluid, by incorporating 1-100 nm nanoparticles in the reference fluid. The incorporation of solid particles is an effective approach for improving the thermal conductivity of suspension due to the higher thermal conductivity of solid as compared to pure liquid [5]. Various metallic and carbon-based nanoparticles have been incorporated for the preparation of nano-fluids [6]. The carbon-based nanoparticles found great attention of researchers due to its excellent thermo-physical properties; hence the number of studies has been performed for use of graphite nanoparticles, fullerene, carbon nanotubes, graphene oxide nano-sheets, graphene nano-sheets [18], graphene copper nanofluid [19], and carbon fibres in energy storage and thermal applications [7]. Ijam et al [8]. The authors

observed the enhancement in the thermal conductivity by 10.47%, while the reduction in the dynamic viscosity of nanoparticles by up to 35% linearly. Sarsam et al [9] studied the thermal properties of graphene/water nano-fluid in the presence of tri-ethanol-amine at various concentrations [16, 17].

In the present study, nano-graphite powder was synthesized from graphite powder and its surface was modified using a strong H₂SO₄ and HNO₃ acid mixture. The UV-Visible spectroscopy was used to investigate of optical characteristics. The thermal properties of NG/water and ANG/water nano-fluids were examined to check its applicability as a thermal fluid. Thermal diffusivity, thermal conductivity and volumetric heat capacity of the nano-fluids have been measured in the mass fraction range 0 – 0.053 wt% and at temperature range of 20 – 80°C.

2. MATERIALS AND EXPERIMENTAL

2.1 Materials

Graphite powder (size < 20 μm), concentrated sulfuric acid (H₂SO₄, 98%), concentrated nitric acid (HNO₃, 98%), ethyl alcohol (C₂H₅OH, 99.9%) and other chemicals required were procured from the standard supplier.

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2.2 Preparation of Nano-graphite and Acid Modified Nano-graphite

The Nano-graphite was synthesized by the co-precipitation method followed by treating with acid to prepare Acid Modified Nano-graphite according to our previous work [10-11].

2.3 Preparation of NG/Water and ANG/Water Nano-fluids

Nano-fluid preparation processes have a big impact on the nanoparticle dispersion in the reference fluid [12]. The creation of a stable nano-fluid is a major challenge for nano-fluid applications. Nano-graphite/water and acid modified nano graphite/water nano-fluids were prepared in two steps. The nano powder was first disseminated in the water, then stirred and ultra-sonicated. The mass of the nanoparticles was calculated at various concentrations as per Eq. 1. The nano-particles were weighed using a digital scale with a least count of 0.001g.

$$Wt. (\%) = \frac{m_{ANG}}{m_{ANG} + m_{H_2O}} * 100 \quad (1)$$

2.4 Characterization Techniques

2.4.1. Morphology, XRD, FTIR and Raman Spectroscopy

The morphological properties, crystal structure and the functional group analysis of prepared NG and ANG, nanoparticles were studied using the SEM, HR-TEM, XRD, FTIR and Raman spectroscopy which were reported in our previous work [10-11].

2.4.2. UV-Visible Spectroscopy

The optical characteristics of NG and ANG nanoparticles were evaluated using UV-Visible spectroscopy (Perkin Elmer, USA) with a spectrum range of 200 – 500 nm.

2.4.3. Thermal Analysis

The thermal properties of the NG/water and ANG/water nano-fluids were measured using the KD-2 Pro-thermal property analyzer (KD2, Decagon Devices, WA, and USA) which is based on the transient hot-wire technique. The thermal properties nano-fluids were evaluated at temperature range of 20 – 80°C. The experiments were repeated five times and the average values were reported in this paper.

3. RESULTS AND DISCUSSION

3.1 Morphological Study, X-ray Diffraction and Raman Spectra of NG and ANG

The NG particle size in some of the layers may reach 400 – 500 nm. The nanoparticle size of produced ANG ranges from 1 nm to 100 nm according to our previous

study [10-11]. The crystal structures of synthesized NG and ANG were determined using XRD to validate the interlayer gap. The micro structural information about conjugated and carbon-carbon bonds in NG and ANG was investigated using Raman spectroscopy. The different functional groups of acid-modified nano-graphite were investigated using FTIR spectra as reported in our previous work [10-11].

3.2 Optical Properties of NG and ANG

As illustrated in Fig. 1, optical extinction spectra from 2-4 times diluted solutions of NG and ANG with the same weight content of 0.0125 mg/ml were recorded in a conventional manner.

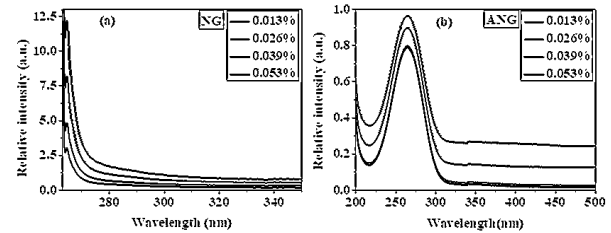


Fig. 1 – Ultraviolet-visible (UV-Vis) spectrum of (a) NG, (b) ANG

It is evident from the figure that the NG peak in both cases has impressive amplitude (optical absorption) and a distinctive form with intricate two-band Gaussian structures. The ANG is most likely caused by distinct nanoparticle aggregations in suspension, resulting in at least two separate kinds of aggregates in water. The UV-visible spectra of an NG and ANG solution that was synthesized in water are displayed in Fig. 1. For NG and ANG, the greatest absorption peak, which indicates the $\pi \rightarrow \pi^*$ transition of the aromatic (conjugation) C-C bonds, was found at 264.54 nm and around 265 nm, respectively. The inclusion of carbonyl groups in the acid-modified nano-graphite results in the $n \rightarrow \pi^*$ transition being indicated by an additional, minuscule shoulder peak at around 341 nm.

3.3 Thermal Conductivity

The thermal conductivity of NG and ANG/water nano-fluid were measured at different concentration and also at various temperatures of 20 – 80 °C.

3.3.1. Effect of Temperature

Fig. 2 (a) and (b) show the thermal conductivity of prepared NG/water and ANG/Water nano-fluids varies with temperature at various concentrations.

The result reveals that, the value of thermal conductivity increased as temperature for all the nano-fluids. At higher temperature, the change in slope increases considerably, showing that effect of temperature has a greater impact on thermal conductivity. The improvement in thermal conductivity as a function of temperature may be because of Brownian motion of

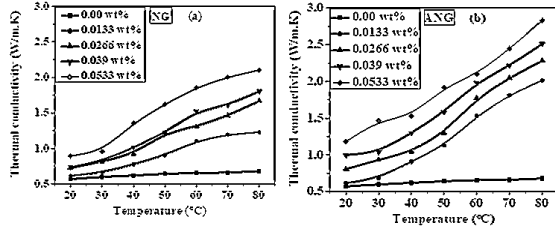


Fig. 2 – Thermal conductivity of nanofluid with temperature (a) NG/water nano-fluid (b) ANG/water nano-fluid

nanoparticles inside the base fluid [13], which causes the nano-kinetic fluid's energy to increase as the temperature rise [14]. The enhancement in the thermal conductivity related to the base fluid was calculated by Eq. 2.

$$\text{Thermal Conductivity enhancement (\%)} = \frac{k_{nf} - k_f}{k_f} * 100 \quad (2)$$

Where, k_{nf} and k_f are the thermal conductivities of the Nano-fluid and base fluid respectively.

Table 1 shows the improvement in thermal conductivity for both the NG/Water and ANG/Water nano-fluids with the temperature. The temperature shows the great impact on the value of thermal conductivity for both types of nano-fluids. The thermal performance as a function of temperature suggested that nano-fluid can be used in actual practice. As the heat load on the components increases, the thermal efficiency of the nano-fluid improves automatically at higher temperatures.

Table 1 – Enhancement in thermal conductivity of the NG/Water and ANG/Water nano-fluids with the temperature

Temperature(°C)	TCE of NG/water nanofluid (%)	TCE of ANG/water nanofluid (%)
20	36.17	51.612
30	37.36	59.044
40	54.27	59.278
50	60.33	66.527
60	64.56	68.66
70	67.13	73.028
80	67.64	75.97

3.3.2. Effect of Mass Fraction

Fig. 3 shows the effect of nanoparticle concentration on the value of thermal conductivity of the nano-fluids at various temperatures.

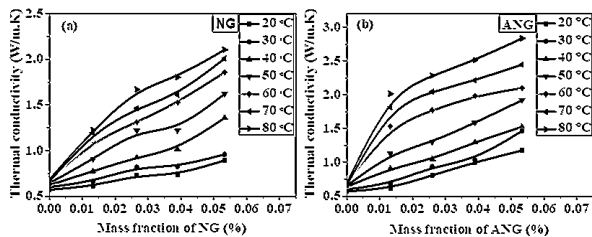


Fig. 3 – Thermal conductivity of nano-fluid as function of mass fraction (a) NG/water nano-fluid, (b)ANG/water nano-fluid

From the figure it can be seen that the thermal conductivity of the nano-fluid is more than water and value of thermal conductivity increases with NG and ANG concentrations. The rise in the concentration of nanoparticles causes positive variations in the thermal conductivity of nano-fluid caused by the increase in the physical interactions between the nanoparticle and base fluid. From the graph, it can be concluded that thermal conductivity of ANG/water nano-fluid is higher than that of NG/water nano-fluid, due to ANG have high surface area and delocalized electron pair. Based on the results, it can be concluded that using nano-fluid at higher temperatures and appropriate concentrations provides the better efficiency. Table 2 shows percentage improvement of thermal conductivity concerning the mass fraction at various temperatures.

Table 2 – Thermal conductivity enhancement (TCE) of NG/water and ANG/water nano-fluids as a function of mass fraction at 80°C

Mass fraction (wt %)	TCE of NG/water nano-fluid (%)	TCE of ANG/water nano-fluid (%)
Base Fluid (Water)	0	0
0.01	44.45	66.186
0.02	59.19	70.17
0.03	62.25	72.9
0.05	67.64	75.97

The results indicate that enhancement in the thermal conductivity is more pronounced at lower temperature and mass fraction of nanoparticles has more impact on thermal conductivity enhancement than temperature.

3.4 Thermal Diffusivity

The thermal diffusivity and thermal conductivity are related as $\alpha = k/Cp$. Where α indicates thermal diffusivity, k indicates thermal conductivity, ρ indicates density, and Cp indicates heat capacity. The specific volumetric heat capacity of the nano-fluid has been determined as ρCp [15].

3.4.1. Effect of Temperature

The thermal diffusivity of the nano-fluids decreases the thermal diffusivity of the nano-fluids decreases with an increase in temperature at all mass fractions of NG and ANG nanoparticles, as shown in Fig. 4.

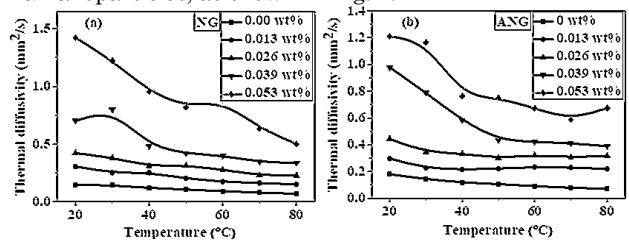


Fig. 4 – Thermal diffusivity of nanofluid with temperature (a) NG/water nano-fluid, (b) ANG/water nano-fluid

As temperatures rise, higher energy electrons become thermally populated, increasing electron-electron scattering resulting decrease in the thermal diffusivity [15]. Fig. 4 (a) and (b), the thermal diffusivity of the NG and ANG/water nano-fluid decreases from 1.4297 to 0.50119 mm²/s and from 1.21069 to 0.67476 mm²/s respectively, when the temperature is increased from 20 to 80 °C at 0.0533 wt%.

3.4.2. Effect of Mass Fraction

The thermal diffusivity of the nano-fluids was measured at different mass fraction from 0 to 0.053 wt%. At all temperatures, the thermal diffusivity of the NG and ANG/water nano-fluids increase with an increase in the mass fraction, as shown in Fig. 5.

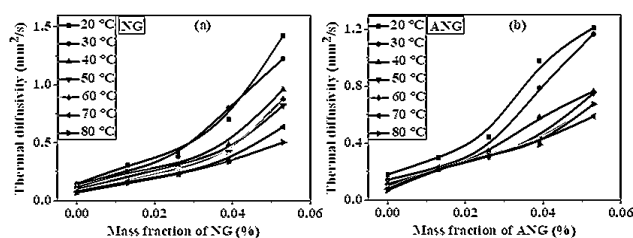


Fig. 5 – Thermal diffusivity of nano-fluid with mass fraction (a) NG/water nano-fluid, (b) ANG/water nano-fluid

ANG/water nano-fluid shows higher thermal diffusivity compared to the NG/water nano-fluid at any mass fraction due to the higher surface area and thermal conductivity of ANG.

3.5 Volumetric Heat Capacity

The volumetric heat capacity of the NG/water and ANG/water nano-fluids at different mass fraction from 0 % – 0.053 % of NG/ANG and as a function of temperature have been studied in this work.

3.5.1. Effect of Temperature

Fig. 6 shows the effect of temperature on the heat capacity of NG/water and ANG/water nano-fluids.

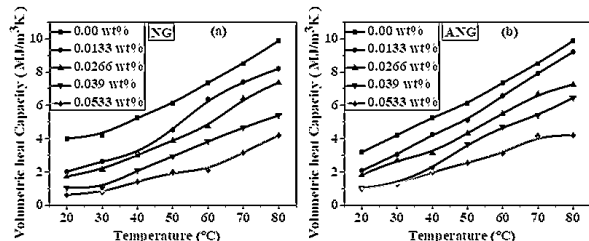


Fig. 6 – Volumetric heat capacity of nano-fluid as function of temperature (a) NG/water nano-fluid, (b) ANG/water nano-fluid

The volumetric heat capacity of the nano-fluid increases by increasing temperature. The change in slope is significantly larger at higher temperatures and improved volumetric heat capacity makes a significant

contribution to practical applications. Fig. 6 (a) shows the volumetric heat capacities of NG/water nano-fluid as a function of temperature which increases from 0.628 to 4.2 MJ/m³K for 0.053% mass fraction. Fig. 6 (b) shows the volumetric heat capacities of ANG/water nano-fluid increases from 0.973 to 4.2 MJ/m³K for 0.053% mass fraction as a function of temperature. The result shows that changes in the temperature greatly influence the volumetric heat capacity of nano-fluids. The volumetric heat capacity of ANG/water nano-fluid is greater than the volumetric heat capacity of NG/water nano-fluid because ANG/water nano-fluid contains acid group, due to which more energy is required to reach a certain temperature.

3.5.2. Effect of Mass Fraction

The volumetric heat capacity of the nano-fluids at different concentrations of NG/ANG is shown in Fig. 7 (a) and (b). The volumetric heat capacity of the nano-fluids decreases with an increase in the nanoparticle concentration. Physical interactions in the nano-fluid environment are only responsible for the negative changes in volumetric heat capacity caused by higher concentration. The phenomena of mixing will increase as the number of nanoparticles inside the base fluid increases due to Brownian motion [13], resulting in a considerable fall in the heat capacity of the nano-fluid when compared to water. With increasing the mass fraction of nanoparticles, the thermal energy is transported easily and less energy is required for excitation of the nano-fluid resulting in a decrease in volumetric heat capacity.

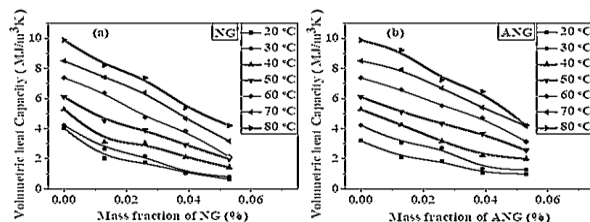


Fig. 7 – Volumetric heat capacity of nano-fluid as function of mass fraction (a) NG/water nano-fluid, (b) ANG/water nano-fluid

4. CONCLUSION

The objective of this research was to enhance the thermal properties of a fluid (water) that has a wide range of industrial uses. The effect mass fraction of nanoparticles on the thermal properties of nano-fluids has been measured over a broad temperature range. From UV-Visible spectroscopy, it can be observed that $\pi \rightarrow \pi^*$ transition of the aromatic (conjugation) C-C bonds showed at about 265 nm. With a rise in temperature and mass fraction of NG/NG, the thermal conductivity of NG/water and ANG/water nano-fluids increases. The volumetric heat capacity of nanofluids increases with temperature whereas decreases an increase in the mass fraction of NG and ANG. Because graphite has a higher intrinsic thermal conductivity than pure water, nano-

graphite and acid modified nano-graphite loaded water has a superior thermal performance than pure water. Hence NG/water and ANG/water nano-fluids can be used in high cooling devices such as solar cells, micro-electronics, nuclear systems, automobile engines, and industrial processing.

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Вплив модифікації поверхні, температури та масової частки на теплові властивості нанофлюїду нанографіту/води

B. Pratap¹, G. Sahu², S.P. Mahapatra¹

¹ Department of Chemistry, National Institute of Technology, 492010 Raipur, Chhattisgarh, India

² Department of Mechanical Engineering, Government Engineering College, 492015 Raipur, Chhattisgarh, India

Наночастинки нанографіту (НГ) і кислотно-модифікованого нанографіту (КНГ) були синтезовані з порошку графіту з використанням сильної кислоти, тобто суміші (сірчаної кислоти та азотної кислоти). Оптичне дослідження та стабільність нанофлюїдів НГ і КНГ/вода були визначені за допомогою вимірювання ультрафіолетової спектроскопії. Теплові властивості, включаючи теплопровідність, температуропровідність та об'ємну теплоємність нанофлюїдів, вимірювали в діапазоні масової частки 0–0,053 мас.% і в діапазоні температур 20–80 °C. Теплопровідність і теплопровідність нанофлюїдів демонструють значне зростання, тоді як об'ємна теплоємність зменшується з концентраціями НГ і КНГ. Поліпшення теплопровідності нано-рідин демонструє значне зростання, з максимальним збільшенням на 67,64 % і 75,97 % для навантажень 0,053 мас. % НГ і КНГ відповідно. Об'ємна теплоємність нанофлюїдів зменшується зі збільшенням масової частки НГ і КНГ і збільшується з підвищенням температури. Як наслідок, наночастинки НГ більш ефективні для підвищення теплопровідності нанофлюїдів на водній основі, ніж частинки КНГ за вказаних вище навантажень масової частки. Нарешті, на основі отриманих даних, з точки зору теплових характеристик у практичних системах, нано-рідини можна визначити як життєздатну альтернативу рідинам на водній основі.

Ключові слова: Синтез, Нанографіт, Модифікація поверхні, Нанофлюїди, Термічні властивості.