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THERMOPHYSICAL PROPERTIES OF NANOFLUIDS CONTAINING MULTI-WALLED CARBON NANOTUBES (MWCNT)

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Abstract. *This work aims to evaluate the synthesis and characterization of nanofluids of carbon nanotubes of multiple walls (MWCNT) functionalized with -OH in distilled water. For this, the thermophysical properties of these nanofluids were measured: thermal conductivity and dynamic viscosity under various temperatures (20-50 ° C) and concentration range of 0.005 to 0.01% by volume. Increases in dynamic viscosity and thermal conductivity of 9.3% and 4.7%, respectively, were found for volumetric concentration of 0.01% at the temperature of 30°C.*

Keywords: *nanofluids, synthesis, thermal conductivity, dynamic viscosity.*

1. INTRODUCTION

Nanofluids are composed of colloidal dispersions with a traditional coolant as a base on which the nanoparticles are suspended. They became part of the scientific scenario in 1995, when researcher Stephen US Choi and his collaborators aimed to improve the heat transfer process for optical elements of high-flow X-ray apparatus in Argonne National Laboratory and reported significant improvements in heat transfer performance (Choi et al., 1995).

In one of the pioneering works (Masuda et al., 1993) dispersed ultrafine particles of Al_2O_3, SiO_2 and TiO_2 in a base fluid using electrostatic repulsion obtaining an increase in the thermal conductivity proportional to the concentration. Ultrafine particles or nanoparticles, with sizes between 1 and 100 nanometers (nm) (1nm = 10-9m) have distinct physical and chemical properties when compared to the properties of particles with the same materials.

In view of energy security and environmental concern, the performance of coolant system needs to be improved, which can be done by modifying the systems or properties of the primary and secondary working fluids. Recently, nanofluids or hybrid nanofluids have gained interest in many engineering fields because of their excellent thermophysical properties, which can be easily used in refrigeration and air conditioning systems for many performance enhancing functions.

The nanofluid technology offers a high potential for controlling the heat transfer systems and increasing heat exchange efficiency in small volumes. Fluid properties can improve with addition of nanomaterials. In some cases, such as where it is necessary to transfer high thermal flux from the solid environment to the fluid, existing methods such as modifying the fluid dynamics, flow geometry alone could not handle the rising energy control demand in existing processes. Accordingly, it is necessary to increase the efficiency of these applications while optimizing energy consumption and decreasing operating costs (Moradi et al., 2019).

Due to energy security and environmental concern, the coolant systems performance needs to be improved, which can be done by modifying the systems or properties of primary and secondary working fluids. Recently, nanofluids have gained interest in many engineering fields because of their excellent thermophysical properties, which can easily be used in refrigeration and air conditioning systems for many performance enhancing functions (Bhattad et al., 2018).

Thermal conductivity is directly related to heat transfer capabilities of fluids, viscosity governs the ease of flow, pressure drop and consequent pumping power involved during the transport (Suresh et al., 2012). Thermal conductivity of nanofluids varies with the size, shape, and material type of nanoparticles. For example, nanofluids with metallic nanoparticles were found to have a higher thermal conductivity than nanofluids with non-metallic (oxide) nanoparticles. The smaller the particle size, the higher the thermal conductivities of nanofluids. Furthermore, nanofluids with spherical shape nanoparticles exhibit a smaller increase in thermal conductivity compared with the nanofluids having cylindrical (nano-rod or tube) nanoparticles (Sanchez et al., 2005).

2. STABILITY OF MWCNT/WATER NANOFLUIDS

Even in the advancement of technological methods to prepare nanofluids, there is still difficulty to make an ideal nanofluid without the formation of agglomerates, which causes the settlement and clogging in micro heat transfer devices. The aggregation of nanoparticles in host fluids mostly occurs due to the strong Van der Waal forces and high surface areas among the nanosized powder, and sedimentation resulting in the density difference between the nanoparticles and base fluid (Arshad et al., 2019). Thus, a dispersion is a central problem to ensure that the use of NTC occurs at the nanoscale and with an effective transfer of its properties to the products of interest (Zhu et al., 2007).

The stability of nanofluids depends on the characteristic of depressed nanoparticles and base fluids. According to Stokes's law, the sedimentation velocity (V_{sed}) as formulated from Eq. (1):

$$V_{sed} = \frac{r^2(\rho_{np} - \rho_{bf})g}{9\mu} \tag{1}$$

Here, r^2 is the radius of dispersed particle, ρ_{np} and ρ_{bf} are the densities of nanoparticle and base fluid respectively, g is the gravitational acceleration, and μ is the dynamic viscosity of the nanofluid. From Eq. (1), it can be seen that V_{sed} decreases with decreasing size of nanoparticle and the density difference of nanoparticle and base fluid and increasing viscosity of the base fluid.

Post synthesis NTCs are highly agglomerated and have low dispersibility in any type of solvent. This agglomeration is due to the occurrence of van der Waals forces between nanotubes, leading to bundles. Thus, depending on the intended applications, there is a need to break down these clusters and obtain the NTCs in their isolated state or dispersed in liquid medium via functionalization. The NTC functionalization process consists in modifying the walls, ends or inside of nanotubes by introducing chemical species of interest. This process is crucial for the applications of these nanomaterials, as it opens the perspective to obtain different functionalities (idea of purpose) to these materials, thus allowing the exploration and modulation of their intrinsic physical properties, the obtaining of new properties and the development of multifunctional hybrid systems through chemical modifications (Balasubramanian and Burghard, 2010). In this sense, several approaches to NTC functionalization have been proposed, and based on the nature of the chemical bonds involved we can classify the types of functionalization into: non-covalent and covalent (Sun et al. 2002).

Acid treatments are the most common for the insertion of covalent functional groups into NTC, among other less reported methodologies involving ozone, oxygen plasma or ultraviolet radiation. Treatments generally use nitric (HNO_3) and sulfuric (H_2SO_4) acids in ultrasound, reflux or ultrasound followed by reflux.

Acid treatment mainly involves the formation of carboxylic groups, phenolic hydroxyls, lactones, carboxylic acid anhydrides and quinones, Figure 1. Acid treatment also causes the length reduction of NTC. Non-functional NTCs are more intact (with greater crystallinity and length), but more difficult to disperse. Functionalization results in a reduction in the length of the NTC, but also in a better dispersion (both due to the presence of oxygenated groups and the shorter length). Therefore, functionalization involves a trade-off between dispersion capacity and structural quality of NTC, two parameters of extreme importance for its application (Sun et al., 2002).

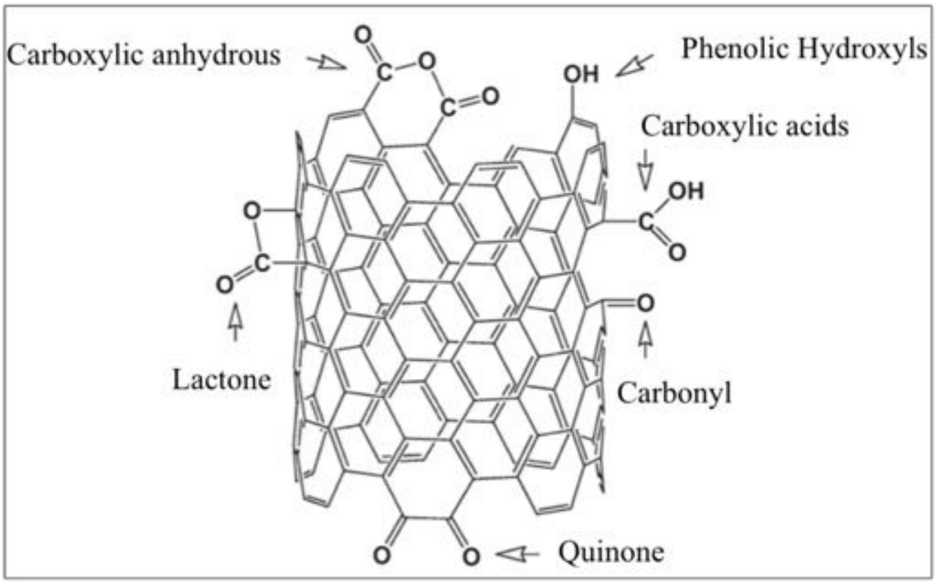

Figure 1. Main oxygenated chemical groups inserted in NTC after acid treatment.
(Salzmann et al., 2007)

3. THERMAL CONDUCTIVITY OF NANOFLUIDS

Thermal conductivity of materials is generally measured by transient or steady state methods. There are several methods for measuring thermal conductivity, for example the thermal comparison method, the 3ω method, the cylindrical cell method, the thermal constant analyzer method, the oscillating temperature method, the steady-state parallel plate method. state parallel plate) and the transient hot wire (THW) technique, the latter being the most used (Li et al., 2009). The THW method has been widely used due to its simplicity of operation, accuracy and speed in obtaining (Paul et al., 2010).

There are many controversial reports in the literature about the thermal conductivity of nanofluids, which is due to behaviors associated with chemistry and physics between nanoparticles and the surrounding fluid that are not fully understood. However, the large number of publications in this area allowed the elaboration of mathematical models to describe certain effects that may be the cause of the anomalous behavior present in the thermal conductivity of nanofluids. Figure 2 lists the main effects that influence the thermal conductivity of nanofluids according to (Arshad et al., 2019).

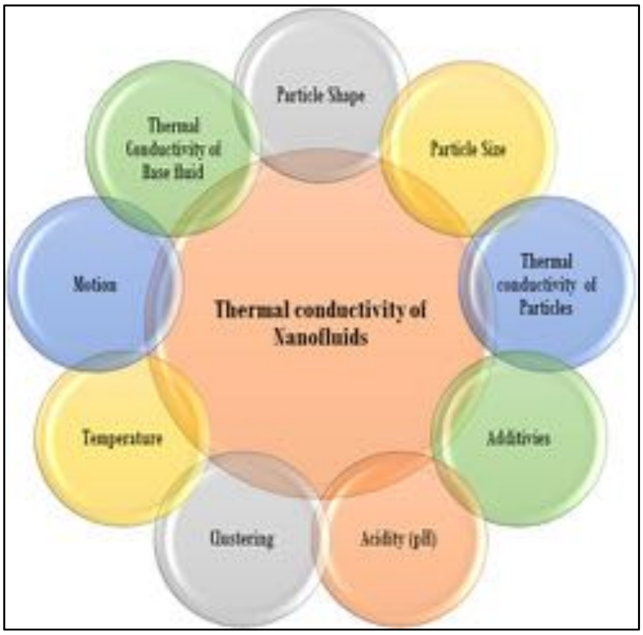

Figure 2. Factors affecting the thermal conductivity of nanofluids (Arshad et al., 2019).

Buongiorno and Hu (2013) , with the aim of to measure the thermal conductivity of various types of nanofluids, it performed a series of measurements at various research centers around the world. In this study, it was found that the thermal conductivity results found by the various researchers were within a ± 10% deviation range, showing the importance of thermal conductivity characterization. They also noted that the thermal conductivity is proportional to nanoparticle concentration and aspect ratio.

4. VISCOSITY OF NANOFLUIDS

Viscosity of the nanofluids is an important parameter on heat transfer performance between the medium because the pressure drop and pumping power depend on it. The effective viscosity of nanofluids depends on the viscosity of the base fluid and volume fraction of the nanoparticles suspended in the fluid. In like manner, other physical parameters like particle size and types of nanoparticles contribute to the effects on viscosity. However the key parameter, temperature, has the significance influence on the viscosity of the nanofluids (Ghadimi et al., 2011). Compared to the works on thermal conductivity of nanofluids, only a few studies have been reported on the rheological behavior of nanofluids.

The viscosity of nanofluids is influenced by several factors, as shown in Fig. 3, such as viscosity of base fluid, volume concentration, morphology, clustering, shear rate and temperature.

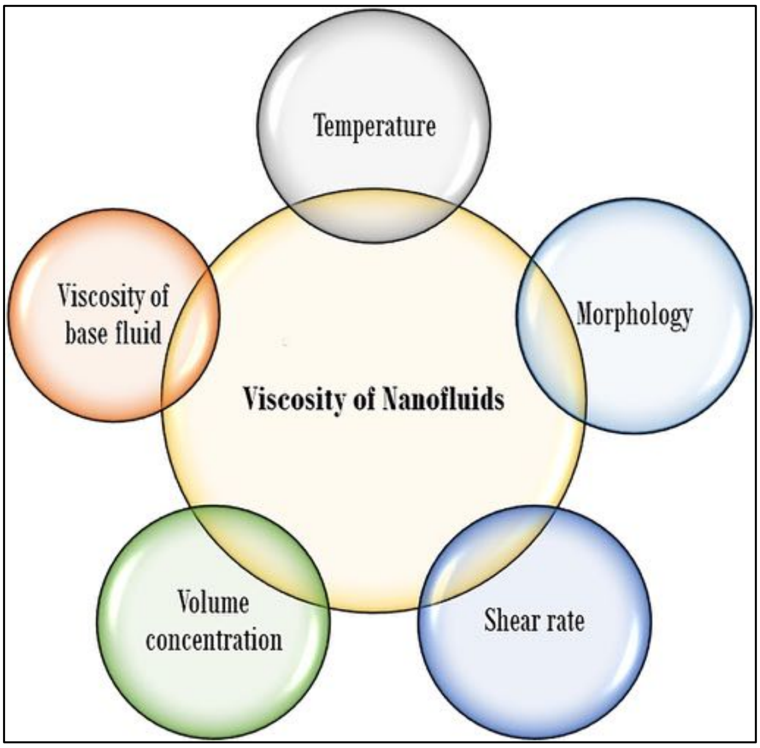

Figure 3. Factors affecting the viscosity of nanofluids (Arshad et al., 2019).

Kang et al. (2006)measured the viscosities of nanoparticles of diamond/ethylene glycol, silver/water, and silica/water nanofluids. They found that the viscosity increase was 50% for diamond/ethylene glycol nanofluid, 30% increase for silver/water and 20% increase for silica/water nanofluids at volume concentrations of 1%, 2% and 3%, respectively. Prasher et al. (2006) demonstrated the viscosity of Al_2O_3/propylene glycol nanofluids was independent of shear rate, proving that the nanofluids are Newtonian in nature and increases as nanoparticle volume concentration increases. They found a 30% increase in viscosity at 3% volume concentration and attributed this increase to aggregation of the nanoparticles in the nanofluid with the size of the aggregates around three times the size of the individual nanoparticles. (Nguyen et al., 2008)experimentally investigated the effect due to temperature and particle volume concentration on the dynamic viscosity for the Al_2O_3/water nanofluid. They found that, in general, nanofluid dynamic viscosity increases considerably with particle volume concentration but clearly decreases with a temperature increase. Their results have revealed the existence of a critical temperature beyond which the particle suspension properties seem to be drastically altered, which, in turn, has triggered a hysteresis phenomenon.

Namburu et al. (2007) presented an experimental investigation of rheological properties of copper oxide nanoparticles suspended in ethylene glycol and water over temperatures ranging from −35 °C to 50 °C to demonstrate their applicability in baseboard heaters in homes, heat exchangers, automobiles and in industrial plants in cold regions of the world.

5. MATERIALS AND METHODS

This work aims to evaluate the synthesis and characterization of nanofluids of carbon nanotubes of multiple walls (MWCNT) functionalized with -OH in distilled water. For this, the thermophysical properties of these nanofluids were measured: thermal conductivity and dynamic viscosity under various temperatures (20-50°C) and concentration range of 0.005 to 0.01% by volume.

The nanoparticles used in this study were purchased by the author from CTNano. A description of the physical and geometric properties provided by the manufacturer of multiwall carbon nanotube nanoparticles (MWCNT) is given in Tab. 1:

Table 1. Specification of MWCNT

Property	MWCNT
Purity	>95%
Average Diameter of Nanoparticles (nm)	10-20
Average Length of Nanoparticles (µm)	10-30
Color	Black
Morphology	Elongated Tube
Melting Point (ºC)	3652
Boiling Point (ºC)	Not Determined
Thermal Conductivity (W/m.K)	5000
Molar Mass (g/mol)	12.01
Density (g/cm^3) at 20ºC	2.1
Specific Heat (J/kg.K)	710
Degree of functionalization -OH wt.%	9%

The preparation of the nanofluids is a rather important step to better the thermal conductivity and dynamic viscosity. There are two most commonly used methods of nanofluid production, the one-step method and the two-step method. The two-step method was used for the development of nanofluids. The synthesis of nanofluids was performed by dispersing MWCNT nanoparticles in distilled water and by homogenization by sonication, as shown in Fig. 2:

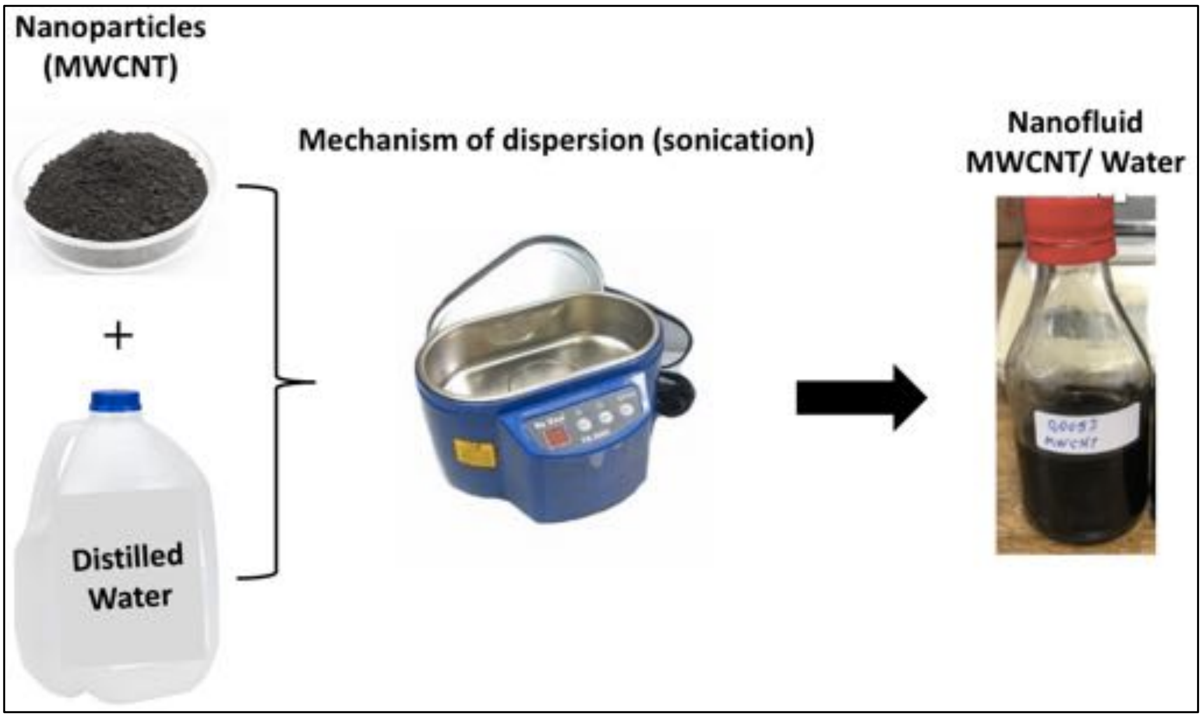

Figure 4. Representative scheme of the two-step method for the synthesis of nanofluids.

The volumetric concentration (φ) of nanofluids was determined using Eq.2:

$$\varphi = \frac{V_{np}}{V_{np} + V_{fb}} \tag{2}$$

Where V_{np} is the nanoparticle volume and V_{fb} is the volume of the base fluid.
Nanoparticle volume can be described as a function of mass according to Eq.3:

$$V = \frac{m}{\rho} \tag{3}$$

Thus, making the relevant algebraic substitutions, the desired nanoparticle mass (m_{np}) for each volumetric concentration is given by Eq.4:

$$m_{np} = \frac{V_{fb} \cdot \varphi \cdot \rho_{np}}{1 - \varphi} \tag{4}$$

Where ρ_{np} is the specific mass of the nanoparticles.

Nanofluid samples with volumetric concentrations (φ) equal to 0.005% were produced; 0.01% and 0.05%, Fig. 3:

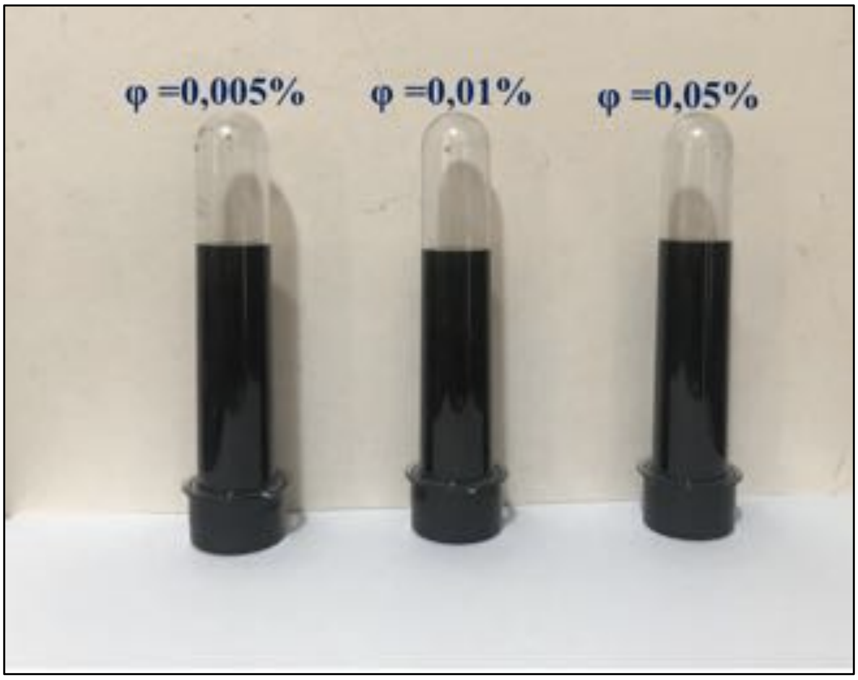

Figure 5. Nanofluids MWCNT/water 24 h after synthesis.

The nanofluids produced were characterized in order to obtain their thermophysical properties: viscosity and thermal conductivity. For these measurements, an Anton Paar SVM 3000 viscometer and a Linseis brand THB-1 thermal conductivity meter was used. In Figure 2 it is possible to observe in (a) the photograph of the thermal conductivity measuring apparatus and in (b) a photograph of the viscometer used.

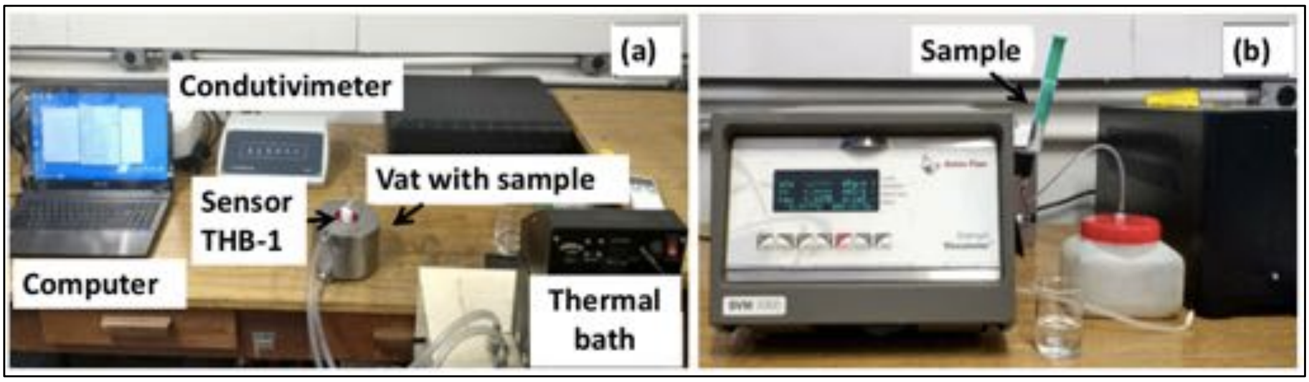

Figure 6. Representative scheme of the Two Step method for the synthesis of nanofluids. (a) image of the experimental apparatus for measuring thermal conductivity, (b) image of the viscometer SVM 3000.

6. RESULTS AND DISCUSSION

According to the results, the addition of MWCNT nanoparticles in distilled water increased both the thermal conductivity and the dynamic viscosity of the distilled water. Since the increase in thermal conductivity was higher than that of viscosity in most of the temperature ranges. Increases in dynamic viscosity and thermal conductivity of 9.3% and 4.7%, respectively, were found for volumetric concentration of 0.01% at the temperature of 30°C. For higher temperatures the increase in dynamic viscosity tends to decrease and that of the thermal conductivity increases. For high temperatures there is significant increase in thermal conductivity with low dynamic viscosity impairment.

The uncertainty of the thermal conductivity and dynamic viscosity measurements was performed by employing GUM method (Jcgm, 2008). The uncertainty $u(x_i)$ can be represented as,

$$u = \sqrt{\frac{\sum_i^n (X_i - \overline{X})^2}{n(n-1)}} \tag{5}$$

in which u is the standard uncertainty, n is sample count, X is the sample thermal conductivity, and $\bar{X}$ is the average of sample thermal conductivity. The uncertainty of thermal conductivity and dynamic viscosity measurements is ± 3% and ± 0.35, respectively.

The thermal conductivity enhancement is defined as,

$$(\%) = \frac{k_{nf} - k_{bf}}{k_{bf}} \times 100 \tag{6}$$

where k_{nf} and k_{bf} are, respectively, the thermal conductivity of nanofluid and base fluid. The dynamic enhancement of viscosity was similarly calculated.

Figure 7 shows the results for thermal conductivity for the MWCNT nanofluids in distilled water.

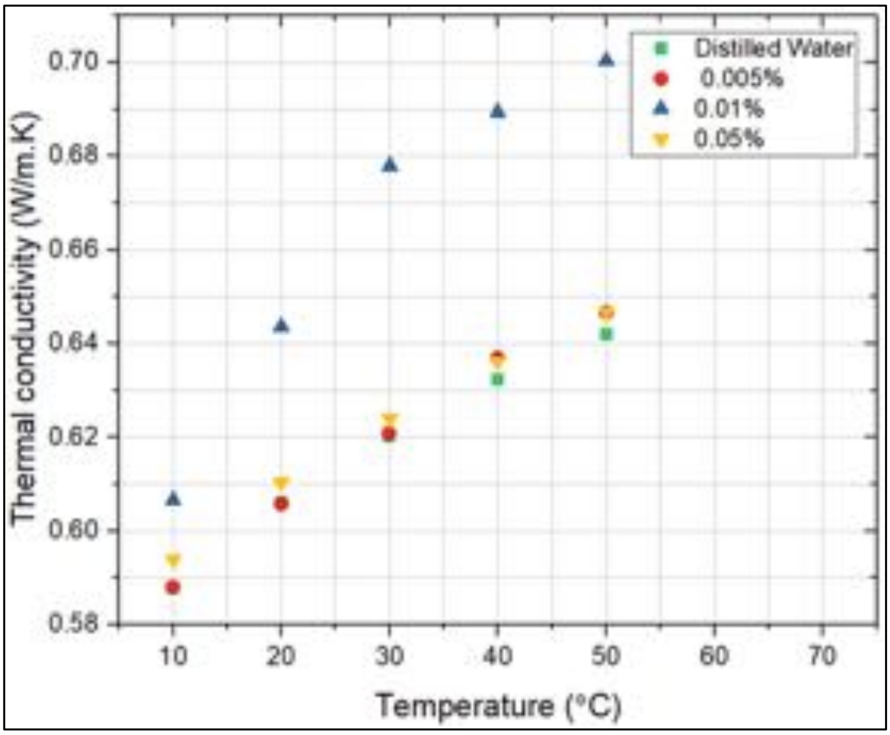

Figure 7. Thermal conductivity for MWCNT nanofluids in water.

Figure 8 shows the increment value obtained for thermal conductivity relative to distilled water.

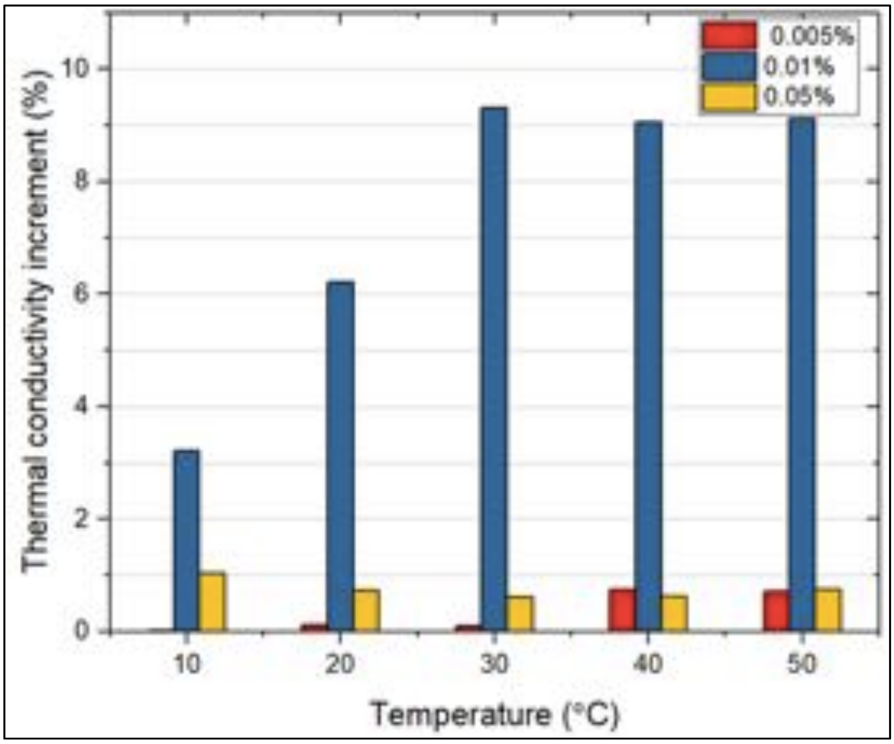

Figure 8. The percentage increase of MWCNT thermal conductivity in relation to distilled water.

Figure 9 shows the results for dynamic viscosity for the MWCNT nanofluids in distilled water.

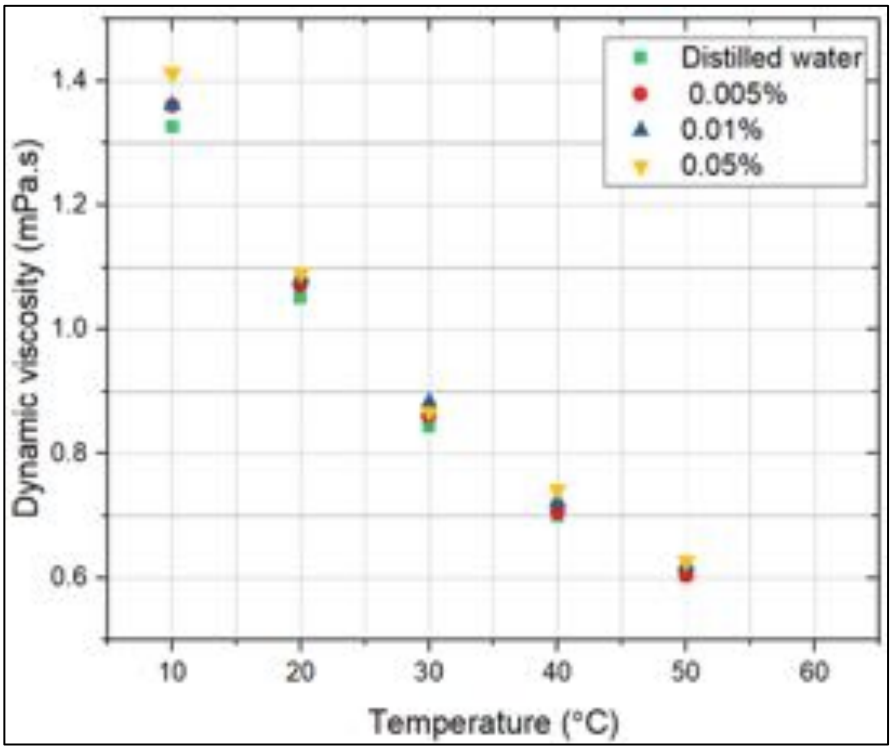

Figure 9. Dynamic viscosity for MWCNT nanofluids in water.

The increase in dynamic viscosity in relation to distilled water was calculated. Figure 10 shows the increment value obtained for dynamic viscosity.

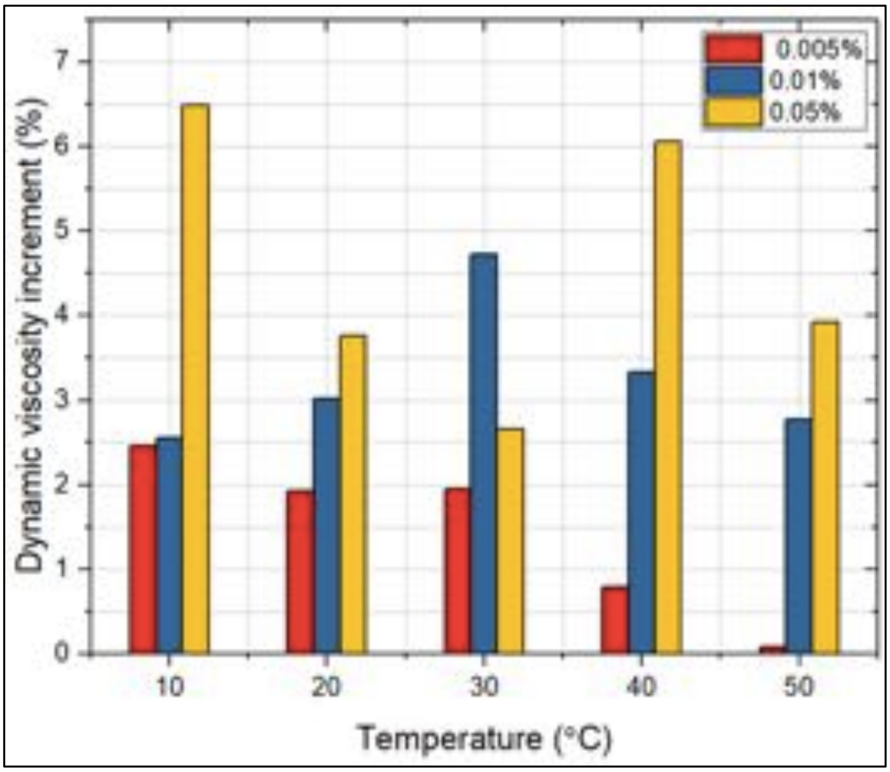

Figure 10. The percentage increase of MWCNT thermal conductivity in relation to distilled water.

7. ACKNOWLEDGEMENTS

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