PREPARATION METHODS OF NANOFLUIDS TO OBTAIN STABLE DISPERSIONS

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Abstract. *With the need for refrigeration systems with great performance and the need for ever smaller devices, to seek alternatives for fluids which have high thermal conductivity. Then one of the studies fronts is nanofluids application. It was verified experimentally that by using conventional fluid with small particles significantly increase the efficiency of conventional fluids such as water. But for these nanofluids have great efficiency is required that the solution is stable, ie no cluster occurrence formation or decanting. This work will then check the stability of nanofluids after being placed in a high-power ultrasonic equipment which produces vibrations in the solution and show dispersal nanofluids methods in the literature.*

Keywords: *Nanofluid, Nanoparticle, Dispersion, Carbon nanotube, deposition.*

1. INTRODUCTION

Nanofluids are fluid formed by dispersing solid particles of size ranging 1-100 nm (nanoparticles) in a given base fluid such as water, for example. Regarding the thermal conductivity, the nanofluids are extremely efficient since the thermal conductivity is increased in relation to the base fluid. However, as expected, these fluids are homogeneous and stable solutions for a short period of time, which in some application, equipment and process is not desired. To mix and prolong the stability is common to use surfactants, which are substances that cause electrostatic repulsion between nanoparticles and the base fluid molecules. The goal of this work is to show some techniques used to obtain dispersions for the production of stable nanofluids, using methods of physical treatment in conjunction with the use of surfactants.

The Fig. 1 depicts the number of publications on nanofluids in the last years, starting in 2000, and as can be observed the significant increment of the publication, including those ones in 2010.

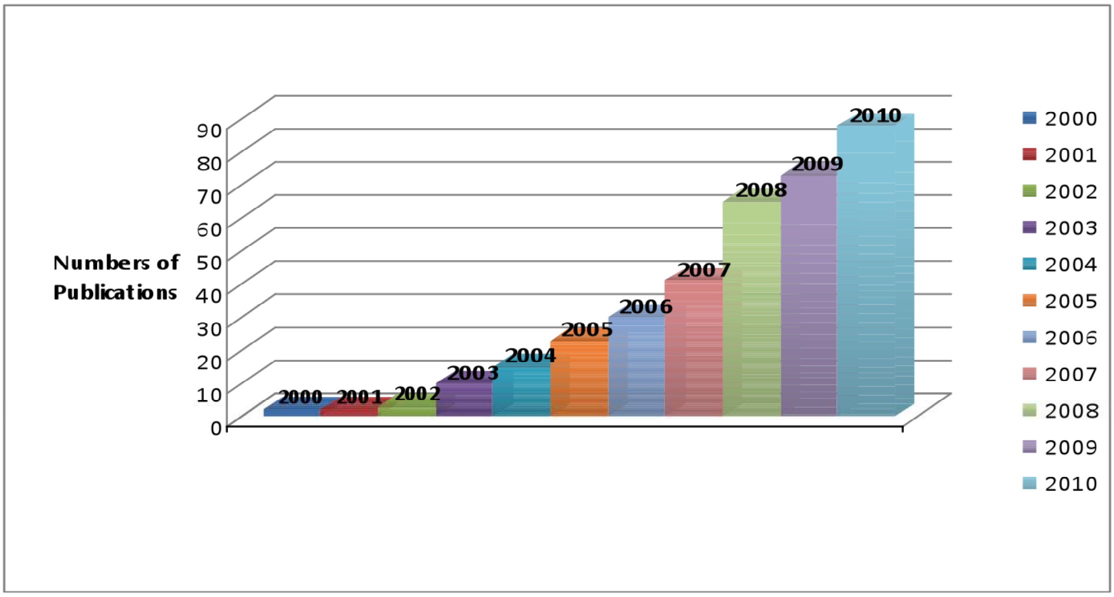
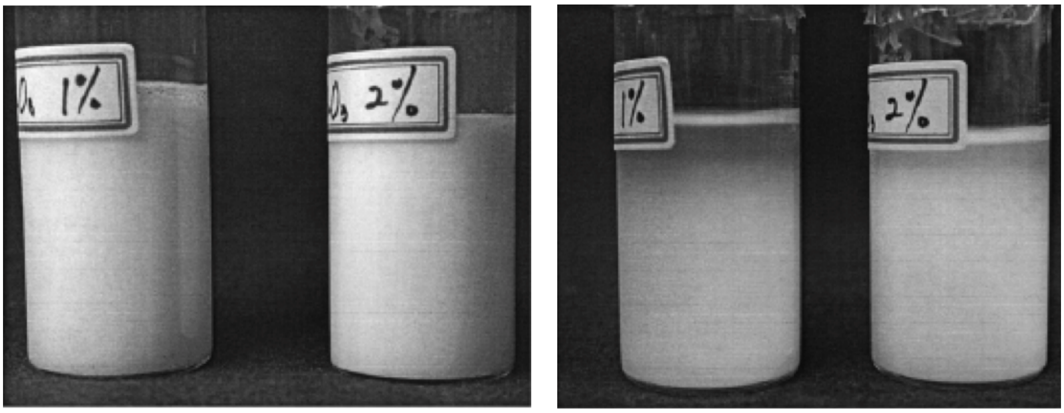


Figure 1 – Number of publications on nanofluids according to the years.

In general, the nanoparticles are insoluble in the base fluids, since the chemical properties and intermolecular interactions between the molecules that constitute the base fluid produce settlements, commonly called "Clusters", after the dispersion.

The thermal conductivity of nanofluids depends on the stability and homogeneity of the solution and with the cluster formation, the thermal conductivity of the nanofluid decreases. The major obstacle of using nanofluids in refrigeration systems and others application is its low stability, which has focused the attention of the scientific community in search techniques for dispersions, which remain homogeneous and stable for a long period. In this paper some techniques currently used, such as: Stirr, Bath Ultrasonic, Sonication, High Pressure Homogenizer and Magnetron Sputtering System will be described. The method used for dispersion in the present work conducted in the Energy and Thermal Systems Laboratory of the Faculty of Mechanical Engineering - UFU was the Sonication.

Lee and Mudawar (2007) conducted experimental tests, analyzing the heat transfer of Al_2O_3 nanofluids flowing in microchannel with 1% and 2% of volumetric concentration. The authors observed that when the nanofluid is not circulating in the system and remain stationary there was a deposition of the nanoparticles, as can be seen in the Fig. 2 (a) and (b). This phenomenon can deteriorate the heat transfer and increase the pressure drop as well as blocking the microchannels. They also not recommended the use of nanofluids in system where operates with phase change, since the decantation of the nanoparticles is much more pronounced in the outlet of the microchannel.



(a) (b)

Figure 2. Deposition of the Al_2O_3 nanofluid. (a) Initial condition and (b) After 30 days.

2. EXPERIMENTAL FACILITY AND METHODOLOGY

Materials and equipment used in the tests were test-tubes (40ml), beakers (1300 ml), carbon nanotubes, base fluids such as ethylene glycol and water, digital scale and sonicator.

There are two methods for the nanofluids preparation: (1) one-step method, where the nanoparticles are generally vaporized and directly dissolved in the fluid base (Ex: Magnetron Sputtering System) and (2) Two Step Method in which nanoparticles are prepared and selected, and finally added to the base fluid to dispersion (Stirrer, Ultra Sonic bath, Sonication and High Pressure Homogenization).

In the experimental tests conducted in this study, the concentrations were taken from 0.1% to 0.5% in both volume and mass. The main reason is that the carbon nanotubes have pores on their surfaces, which causes a volumetric variation and, consequently, varies the density. In these conditions, the densities presented in this work are given as average or approximation provided from the literature and the nanoparticles suppliers, pointing out that percentages by weight are more accurate.

A high-powered facility, known as "Sonic", was used in this work and is presented in the Fig. 3. This facility operates with compressed air and requires a pressure of 600 kPa. The machine provides a frequency of 20 kHz and amplitude of 22.5 micrometers and is composed by 5 main parts: a pressure controller, an amplitude controller, a system test configuration, a frequency controller and a head, depicted in details in the Fig. 4. The head moves both up and down on its own axis and in the upper part is possible to observe the load cell, which transfers vibrations to the tip, promoting the dispersion of the solution.

Figure 3. Facility used in the Sonication method.

Figure 4. Detail of the head of the Sonication Facility.

The tests are conducted by two-step procedure method, in other words, adding nanoparticles in a fluid base. The first tests will be performed only with nanoparticles called carbon nanotubes (diameter of 20-40 nm and length of 5-15μm) with the relation between length and diameter of 500. The base fluid used was distilled water (density of 0.998203 g/cm^3 at 20 ºC) and the solution had concentration of 0.2% by weight. First, was utilized a precision balance to define the mass used in the test. After, distilled water was placed in a beaker and added the nanoparticles. The beaker was placed on the base of the structure just below the tip of the head and the equipment was powered and made all adjusts for the test. After the parameters were properly adjusted such as the pressure, amplitude and frequency, the fine adjust in the head to move until the tip is submerged in the solution and the load cell transfer vibration to the solution.

Thus, after 10 min (or other scale to be specified) the equipment is turned off and the solution is ready to verify if there were cluster formations. The temperature of the solution was also verified during the test using with a thermocouple type T.

3. NANOFLUID ANALYSIS

As mentioned, the nanofluids are colloidal dispersions where the scattered particles have dimensions between 1 and 100 nm, and the particles are generally insoluble in the base fluid dispersed. In these conditions, some properties are presented, as follow.

a) Physical

Suns, the colloidal particle has little affinity for the medium, which will then be unaffected by the presence of such particles. Thus, the colloidal system has physical properties similar to those of the pure dispersion medium.

b) colligative properties

Although the Suns also exhibit colligative properties, its effects are far less pronounced than in the case of real solutions, because the colligative properties are closely related to the number of particles present (the higher this number, the greater the effects of these properties), which is lower in colloidal systems. Still, the Suns showed a small decrease in melting temperature and a small increase in boiling temperature compared to pure dispersion medium.

c) Optical Properties

One of the most important properties of colloidal systems is the scattering of light that occurs when it passes through these systems, called the Tyndall effect. This scattering of light was studied by Gustav Mie, who discovered that she is dependent on the diameter of the particles in the system. Thus, these properties are applied in determining the diameter of colloidal particles, considering them spherical, isotropic and without mutual interaction.

d) Electrical properties

The colloidal particles tend to adsorb on the surface, ions and / or molecules present in a dispersion medium. When it is a sun, the particles attract mainly ions, forming an electrical double layer responsible for the stability of the colloid. For example, if two particles of insoluble material did not have a double layer, they can get close enough so that the attractive force of van der Waals forces may cause them to be together. With double layer of ions to protect them, the particles repel each other at great distances apart, preventing a greater proximity of the particles and stabilizing the colloid. If there is a difference in electrical potential between the adsorbed layers and the dispersion medium, the colloidal particles may migrate toward one pole of an electric field, and you can then slice it in half. Two processes are used in this sense: electrophoresis, which allows the migration of colloidal particles and not the medium, and electroosmosis, which allows the migration of the middle and not the particles.

e) Stability of Colloidal Suspensions

A colloidal suspension is the more stable the lower the tendency for precipitation of colloidal particles. For this precipitation occurs, it is necessary that the colloidal particles to clump together, forming a larger mass that is more susceptible to the action of gravity. Suns, so that precipitation occurs, you must remove the double layer of ions from the surface, and this can be done by adding electrolytes to the medium. This drastically reduces the electrostatic repulsion between the particles and precipitates the colloid. The colloidal particles are particularly sensitive to ions of opposite sign, and the higher its charge, the greater its efficiency in coagulation of the colloid (Rule Schuz-Hardy). Roughly, the minimum concentration of an electrolyte needed to produce rapid coagulation is the reason for the ions 1:10.500 triple, double and single charge.

The colloidal suspensions may also have increased their stability. A sun becomes more stable to adsorb on their surface that has some substance, besides the electric layer, a layer of solvation. This layer is then passed to protect the colloidal particles and also for the occurrence of precipitation, you should also remove this solvation shell, which is only done by adding some substance that has a great affinity for water. The colloidal particles thus protected may have a reversible coagulation, the colloidal system could be regenerated after the precipitation, while the unprotected colloidal particles precipitate irreversibly.

3.1. Method used

The method used in the present work for the nanofluid preparation is known by Titration. This method is a common laboratory method of quantitative chemical analysis that is used to determine the unknown concentration of a known reactant. Since the volume measurements play an important role in titration, it is also known as Volumetric Analysis. The principle of the Tritation is given by:

$$\textbf{Titration (T)} = \frac{\text{Nanoparticles Volume (Va)}}{\text{Solution Volume (Vs)}} \tag{1}$$

Where the titration ranges varies of: $0.001 \le T \le 0.005$ (0.1% to 0.5%)

As **Vs = Va + Vf,** where **Vf** is the volume of base fluid and replacing **Vs** in the Eq. (1),

$$T = \frac{V_a}{V_a + V_f} \tag{2}$$

Rearranging the expression:

$$T(Va + Vf) = Va \Rightarrow T \cdot Va + T \cdot Vf = Va \Rightarrow T \cdot Vf = Va - T \cdot Va \Rightarrow Va \cdot (1 - T) = T \cdot Vf \Rightarrow Va = \frac{T \cdot Vf}{1 - T}$$

Multiplying by the nanoparticles density **(Da)**

$$V_a \cdot D_a = \frac{D_a \cdot T \cdot V_f}{1 - T} \quad ,$$

Finally, the above expression is obtained:

$$M_a = \frac{D_a \cdot T \cdot V_f}{1 - T} \tag{3}$$

Where:
Ma = Nanoparticles Mass
T = Titration
Vf = Volume of the Fluid Base
Da= Nanoparticles Density

As in the experimental procedure adopted T varies from 0.1% to 0.5%, then the area of the quoted expression must be restricted to $0.001 \le T \le 0.005$, was set the volume of fluid based with the value of 10 cm³ and carbon nanotubes density of 1.35 g/cm³ and the silver nanoparticles density of 10,49 g/cm³. The Figs. 5 and 6 depicts the curves showing Ma (T) in function of the Titration for carbon nanotubes and silver nanoparticles.

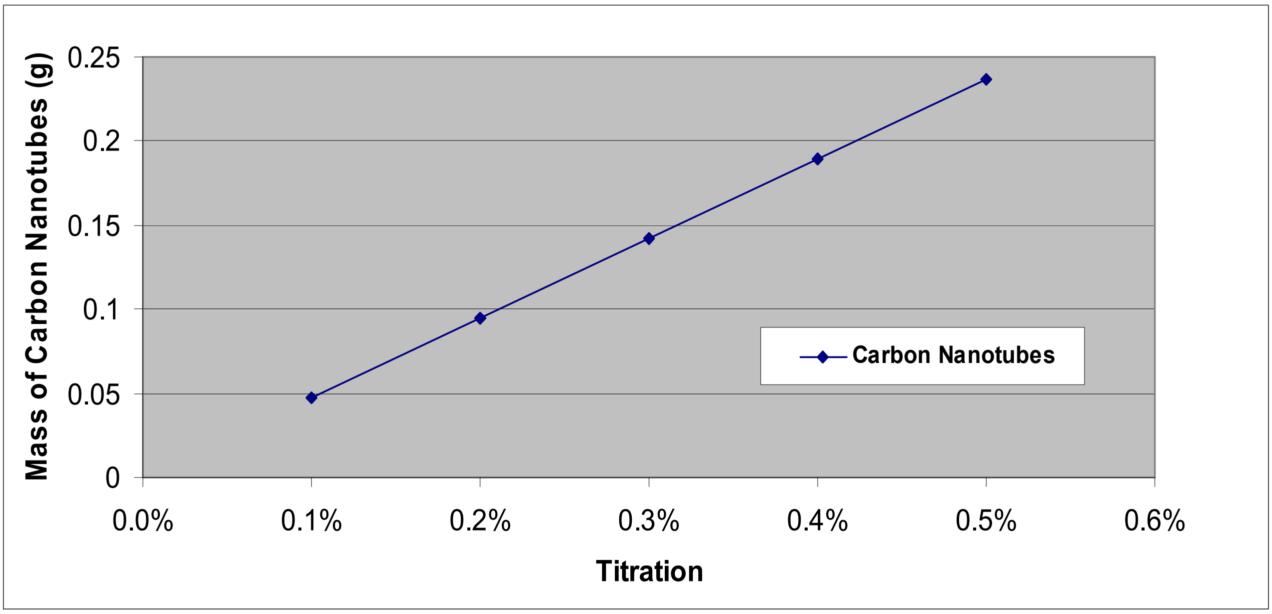


Figure 5. Sample Mass, Ma, in function of the Titration for carbon nanotubes.

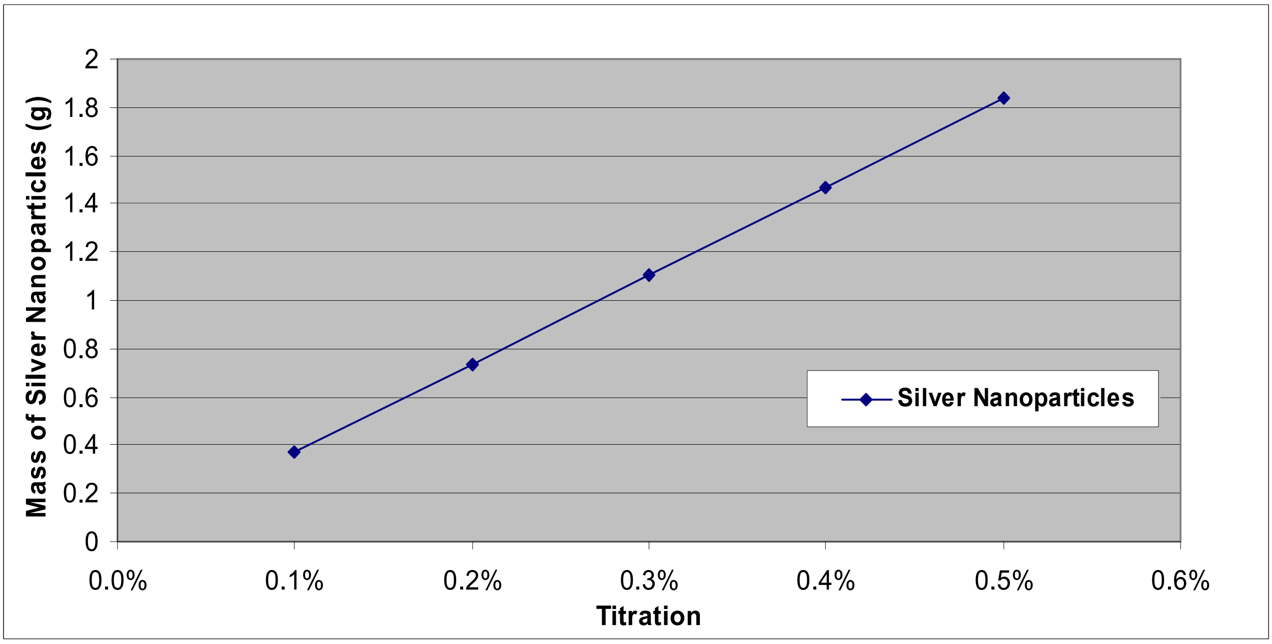


Figure 6. Sample Mass, Ma, in function of the Titration for silver nanoparticles.

As mentioned before, the titration in volume is not so accurate as that one obtained in mass, mainly due to the fact that nanoparticles have pores, which essentially decreases its density and the values presented in this paper are only in mass titration as follow,

$$T = \frac{Ma}{Ma + Mf} \tag{4}$$

Where:
Ma = Mass of Nanoparticles
Mf = mass of fluid base
Rearranging the expression,

$$Ma(T) = \frac{Mf \cdot T}{1 - T} \tag{5}$$

3.2 Methods used in the literature

In the open literature was found some preparation methods to obtain stable dispersions. Some of them used silver nanoparticles (Ag) and carbon nanotubes (CNT), where the base fluid, respectively, were silicone oil and water. In the preparation of these two nanofluids, surfactants were added and then submitted to the physical treatment methods for one step and two steps of dispersion.

For the ultrasonic bath and sonication the process is similar and the main difference between these methods is the medium that the wave propagates. For the sonication the waiting time was 60 min at a frequency of 40 kHz and the power used of 350 W. In this process, the ultrasonic wave is transferred to the sample through water in the bath while the sonication in the spread is made directly to the sample through the sonotrode from the sonicator. After 1 hour of treatment, it was observed considerable changes in the dispersions in which to over time was significantly stable, (Hwang et al. 2007)

The high-pressure homogenizer was the most effective methods among the two steps methods, it consists of two microchannels that divide the feed stream into two other streams and the schematic model is shown in the Fig. 7.

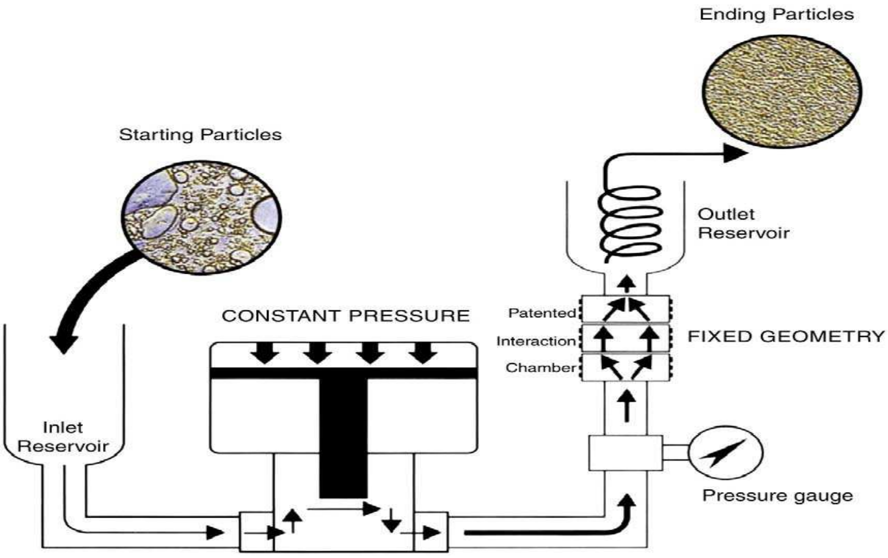


Figure 7. Schematic Model of the High-Pressure Homogenizer. (Hwang et al. 2007)

Both streams are recombined in the reaction chamber, where an increase in the flow rate of the pressurized fluids in the microchannels causes cavities, providing a high-energy cavitation to break the clusters.

In the process, the nanoparticles suspensions flow through of a tube of 3 mm before reaching the interaction chamber. When the suspension reaches the interaction chamber the suspensions flow inside microchannels with a diameter of 75 micrometers. In this condition of contraction flow, the velocity is increased approximately 1600 times according to the Bernoulli's theorem and simultaneously a cavitation phenomenon is occurring. (Hwang et al. 2007)

In the flow region, clusters can be broken by a combination of several mechanisms: (i) strong and irregular impactation with the wall of chamber interaction, (ii) microbubbles formed by cavitation implosion energy and (iii) High shear rate. This leads finally to obtain homogeneous suspensions with many fewer particles bonded with the observation that the experiment was done at a pressure of 124.11 kPa and the samples were taken three times by homogenizing. (Hwang et al. 2007)

The Magnetron Sputtering System is a one-step method used in an attempt to obtain a stable dispersion, shown in Figure 7. In this process, the vacuum inside the chamber is pumped down to fill the chamber with argon gas to obtain a gas pressure desired, with constant flow of Argon gas between 15-50 cm^3/min.

The target substrate is placed in a rotating drum that sits between a reservoir of silicone oil in which the rotation speed varies from 0 to 10 rpm and the distance between the particles of Ag and the drum should be fixed at 8 cm. (Hwang et al. 2007)

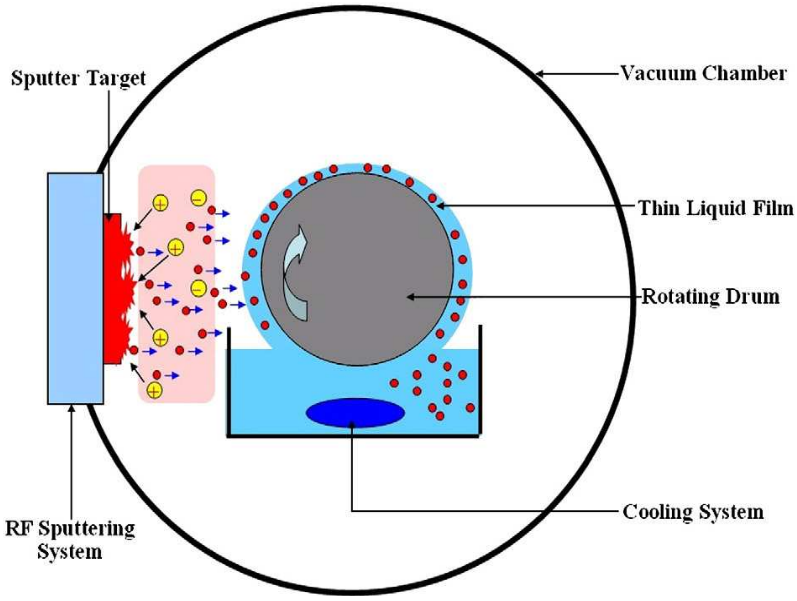


Figure 8. Schematic Model of Magnetron Sputtering System (Hwang et al. 2007)

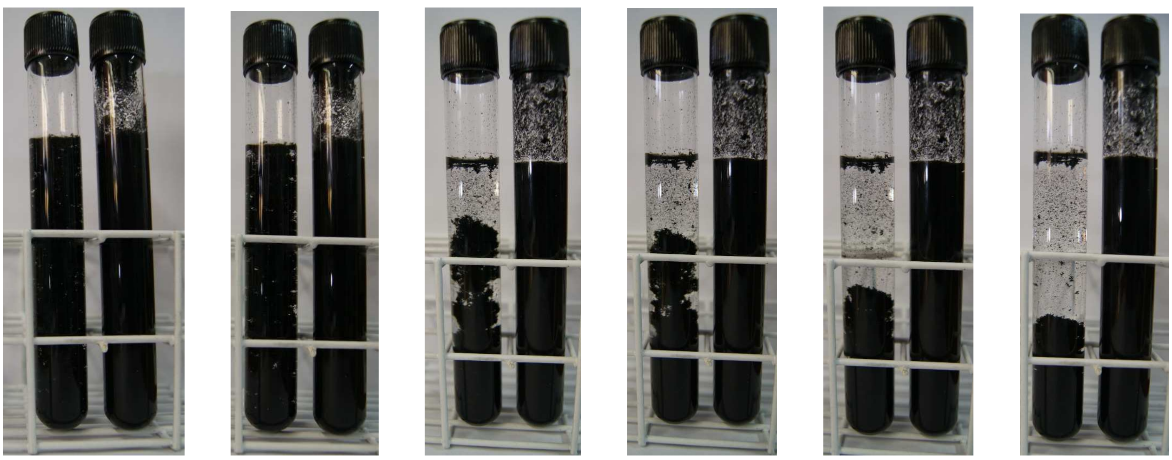
4. EXPERIMENTAL RESULTS

The dispersion process conducted in the present study was the sonication process using carbon nanotubes and the fluid base used distilled water and ethylene glycol. It was observed that is not possible use the sonication process for long time, with the percentage by volume up to 1% using small beaker with volume of 25 cm³, since the thermal conductivity of these nanoparticles are high enough to cause a fast evaporation of the fluid base. An example of this case can be observed in the Fig. 8. It is interesting to note that the nanofluid, prepared with ethylene glycol and carbon nanotubes (left side of Fig. 8), presented very high thermal conductivity and the base fluid (ethylene glycol) was completely evaporated (right side of Fig. 8), remaining only the carbon nanotubes.

For concentration of 0.2% and a volume of 500 ml of distilled water with sonication time of 5 minutes, it was noted that the mixture remained homogeneous in the container, however, when changing to another container it was observed the precipitation of the nanofluid, being visible the phases, forming a two-phase mixture. Increasing the sonication time to 10 minutes, the mixture remained stable even with the transfer to test tubes, which leads the conclusion that as longer as the sonication time better is the stability of the nanofluids. For concentration of 1% and a volume of 10 ml of ethylene glycol, the mixture remained homogeneous and stable for six days, with low precipitation. Experiments using mass percentages should be conducted.

The Fig. 9 shows the behavior of the dispersion after few minutes of sonication process. The left side just contain nanoparticles and base fluid before the sonication process and the right side after the sonication process. It is important to note, even after 2 minutes the nanofluid prepared with the sonication process remaining stable.

Figure 9. Beaker containing the nanofluid dispersion. The left side before the sonication process and right side after sonication process.



t=0 sec t=5 sec t=20 sec t=40 sec t=60 sec t=120 sec

Figure 10. Test-tube containing the nanofluid. The left side just contains nanoparticles and base fluid without the sonication process and the right side after the sonication process in function of the waiting time.

5. CONCLUSIONS

The experiments conducted in the laboratory showed that the sonication process is not effective with a small volume of base fluid and a high concentration of nanoparticles, since that the high thermal conductivity of the solution increased the temperature, causing evaporation of fluid base and leaving only the solid material in the container. Comparing also the sedimentation time of the dispersions, it was observed that the sedimentation of the samples that were not subjected to the sonication process occurred in a shorter time, almost spontaneously, unlike the samples that underwent the procedure that took about four days to decant.

It was possible to conclude, with the experiments and the methods proposed in the literature, that it is possible to obtain stable and efficient nanofluids for many equipment used in both domestic and industrial applications, where the clustering is an obstacle that can be overcome.

With the methods proposed in the literature, the high pressure homogenizer was the most effective method for obtaining stability and homogeneity of nanofluids for a longer period of time, during which its operation provides a higher cavitation energy to break intermolecular forces between the fluid molecules base.

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