

PREPARATION OF COPPER-BEARING NANOFLUIDS FOR THERMAL APPLICATIONS

by

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ABSTRACT

Stable suspension of nanometer solid particles in suitable solvents, so-called nanofluids, has shown enhanced thermal conductivity when compared with the fluid base; therefore, the preparation and characterization of these type of suspension will enable the development of more efficient and effective thermal management systems. In general, nanofluids hosting metal nanoparticles, (e. g., Ag or Cu) would exhibit better thermal conductivities than those bearing oxide nanoparticles. Accordingly, the present research addressed the optimization of the size-controlled synthesis conditions of copper nanoparticles, determination of the most suitable conditions to stabilize those nanoparticles in ethylene glycol and the reproducible measurement of the thermal conductivity as a function of nanoparticle volumetric load. The research work was also focused on the improvement of the stability and reliability of the system used to measure the thermal conductivity of copper-bearing nanofluids.

The synthesis of nanoparticles was achieved through the reduction of copper ions using hydrazine as well as by taking advantage of the reducing power of polyol solutions. The preparation of the copper-bearing stable nanofluid was attempted by treating nanoparticles with surfactant agents to disperse them in the base fluid (ethylene glycol). In the aqueous route, the rate of the Cu reduction reaction and the corresponding average crystallite size of the nanoparticles were strongly dependent on the copper ion and hydrazine concentration. From starting 0.016M Cu solution, the time at which the reduction of Cu was realized was shortened from 12 hours down to only 30 minutes when the concentration of hydrazine was increased from 0.059M to 0.7M. The corresponding average crystallite size decreased from

25nm to 17.8nm. In the polyol approach, the reaction time was as short as 30 seconds when a NaOH/Cu mole ratio = 50 was used. The corresponding average crystallite size, estimated at 21.2nm, went down to 12.7nm when a 5E-7M of Polyvinylpyrrolidone was used. The formation of Copper nanoparticles from starting Cu(II) species, in water and polyol solutions, involved the formation of precursor cuprous oxide (Cu_2O), which underwent dissolution and subsequent reduction into elemental Cu. This dissolution-reduction step controls the average size of nanoparticles of elemental Copper.

The thermal conductivity of nanofluids produced was measured by using the transient hot-wire technique. The relationship between nanoparticle size, volumetric concentration in ethylene glycol and the relative thermal conductivity values are presented and discussed. The thermal conductivity of the base ethylene glycol was increased 32% when copper nanoparticles (7.5 %v/v), averaging 21nm, were suspended in the base fluid.

RESUMEN

Suspensiones estables de partículas sólidas de tamaño nanométrico en solventes adecuados, también llamadas nanofluidos, muestran un incremento en la conductividad térmica cuando se comparan con el fluido base, por tanto, la preparación y caracterización de esos tipos de suspensiones representa una vía para el desarrollo de dispositivos más eficientes para el manejo de calor.

Nanofluidos cuyas partículas sólidas corresponden a metales (como el oro, la plata o el cobre), exhiben en general, un mejor incremento en la conductividad térmica que aquellos nanofluidos preparados con óxidos de escala nanométrica.

Este trabajo fue enfocado en la optimización de las condiciones de síntesis de nanopartículas de cobre para obtener un control de tamaño adecuado, asimismo para determinar las condiciones más adecuadas para la estabilización de las nanopartículas de cobre en etilenglicol, y en la medición de la conductividad térmica de las suspensiones preparadas variando el tamaño y la concentración de las nanopartículas en el fluido base.

Este trabajo también se enfocó en el mejoramiento de un sistema confiable y reproducible de medición de conductividad térmica relativa.

La síntesis de nanopartículas de cobre fue obtenida al utilizar hidracina y etilenglicol, (polyol), como agentes reductores.

En el proceso de síntesis vía hidracina (reducción acuosa), la velocidad de reducción del cobre y el correspondiente tamaño de cristalito de las nanopartículas fue fuertemente dependiente de las concentraciones de hidracina y del Ion de cobre.

Cuando la concentración de las soluciones de cobre fueron de 0.016M, el tiempo de reacción requerido fue reducido de 12 horas a 30 minutos cuando la concentración de hidracina se incremento de 0.059M a 0.7M, del mismo modo, el tamaño promedio del cristalito se redujo de 25.0 a 17.8nm

Utilizando etilenglycol como agente reductor, una solución de acetato de cobre en etilenglycol fue calentada hasta 200°C en presencia de soluciones de hidróxido de sodio con diferente concentracion, cuando la relación entre el numero de moles de hidróxido presente y el numero de moles de cobre presente fue de 50, el tiempo de reacción se disminuyo a treinta segundos, el tamaño de cristalito correspondiente fue de 21.2nm y fue posible reducirlo hasta 12.7nm cuando una concentración de 5E-7M de polivinilpirrolidona fue introducida en la reacción ya descrita.

La formación de nanopartículas de cobre partiendo de iones Cu(II), envuelve la formación de oxido cuproso (Cu_2O), que posteriormente se disuelven y conducen a la formación de cobre metálico, la disolución del oxido cuproso es el paso limitante en la reducción del cobre y esta directamente relacionado con el tamaño promedio del cristalito.

La conductividad térmica de los nanofluidos de cobre fue medida utilizando la técnica del transiente del alambre caliente,

La relación entre el tamaño del cristalito y concentración volumétrica para las nanopartículas de cobre suspendidas en etilenglicol son presentadas y discutidas, el mayor incremento en la conductividad térmica encontrado en este trabajo corresponde a un 32% cuando el tamaño de cristalito fue de 21nm y la concentración volumétrica de 7.5%.

To my family . . .

Dedicated to my lovely parents, my wonderful wife and my friends for bringing me the opportunity of shared with them some of more beautiful moments in my life

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1 INTRODUCTION

More efficient cooling systems become indispensable in different industries, such as the electronic and the automotive ones. Enhanced efficiency in heat management becomes imperative since the heat produced from the operation of mechanical and electronics devices must efficiently be extracted to avoid their own failure or permanent damage. Moreover, the optimum cooling system should be compact enough and easy-to-handle under normal operating conditions.

Stable suspensions of nanometer solid particles in suitable solvents, so-called nanofluids, have shown enhanced thermal conductivity when compared with the fluid base; therefore, these composite materials represent a promising route for efficient and effective thermal management in different systems. From a thermal conductivity viewpoint the literature shows several good examples. Choi *et al.* have reported an increase of 20 percent in thermal conductivity with respect to pure water when 5% v/v of copper oxide nanoparticles was suspended in the fluid [1]. In the case of ethylene glycol as solvent, the same work found a 20% increase in the thermal conductivity when 4% v/v of copper oxide nanoparticles was used. The addition of 1% v/v of copper nanoparticles to water caused a rise in the thermal conductivity of up 40% [2].

The improvement of thermal properties exhibited by these nanofluids is of great technological interest because their commercial use would permit the development of more efficient and cost-effective cooling systems. In the case of electronic industry, for instance, it

is expected that the heat flux produced in VLSI microelectronic components can be increased up to 1000 kW/m^2 . Also, the next generation of computer chips will reach 10 MW/m^2 , a extremely high value when compared to the heat flux in actual microprocessors, ($10\text{-}50\text{W/cm}^2$) [3].

On the above basis, the present work will be focused on: i) the optimization of the synthesis conditions to achieve copper nanoparticles with suitable size and determine a way for shape control (ii) determination of the most suitable conditions to stabilize these nanoparticles in conventional cooling liquids, e.g. ethylene glycol and (iii) measurements of the variation in thermal conductivity in produced nanofluids as a function of nanoparticles load for the optimum synthesis conditions. The synthesis of nanoparticles will be made through the reduction of copper ions in solution media. The conditions of synthesis will be optimized in order to achieve a fine tuning on purity, crystal size and size monodispersity. In turn, the preparation of the copper-bearing nanofluid will be attempted by treating nanoparticles with surfactant agents and dispersing them in the fluid base. A variation in the preparation of the nanofluid consists of synthesizing the nanoparticles in-situ, i.e. inside the base fluid. In this case, the fluid should behave not only as a solvent but also as a reducing agent.

The thermal conductivity of the nanofluids produced will be measured by using the transient hot-wire technique, where a fine wire is immersed in the sample fluid. The wire is used as heater and thermometer. The corresponding calculations are based on a transient line source

model; in this case, the thermal conductivity is related to the slope of the plot of temperature versus time [4].

1.1 Motivation

Heat transfer fluids are commonly used in the cooling systems of electronic devices, transportation machines and manufacturing equipment. The performance of these cooling systems is strongly dependent on the thermal properties of the fluid. Until now, commercially available heat transfer fluids have allowed the development of new mechanical systems and electronic devices; however, the miniaturization of components and development of new and more efficient machines has increased considerably the energy load that should be removed per unit time. Accordingly, the development of a new cooling system based on heat transfer fluids with enhanced thermal conductivity properties becomes indispensable.

One way to increase the efficiency in cooling systems is the development of fluids whose thermal properties are superior to currently used commercial fluids. In this regard, a nanofluid is a stable suspension of nanoparticles with suitable size and size distribution [5], in a heat transfer fluid. The most important feature of the nanofluid is its improved thermal conductivity in comparison with the same fluid but without nanoparticles [6, 7, 8]. This feature is of great industrial importance since the performance of the devices strongly depends on how efficient the heat is managed, inside and outside the systems. Among the nanofluids considered, those that seem to exhibit the best thermal properties are the ones

containing metal nanoparticles [9]. It has been demonstrated that copper, silver and gold-bearing nanofluids exhibit outstanding thermal properties [5, 10, 11, 12] .

Many solids, metals in particular, report thermal properties that exceed in several order of magnitude the properties of the fluid alone; however, fluids are easier to handle that facilitates their use in cooling devices such as the micro-channel system cooling [13]. Although the idea of using fluids bearing metallic particles is not quite new, (fluids with micron-size particles were used in the past but the results were not the expected ones [9, 10], due to uncontrolled aggregation of particles), to the best of our knowledge, there is a lack of systematic efforts oriented to investigate the effects of nanocrystal size and size monodispersity on the thermal properties of the corresponding fluids. Ongoing studies using nanoparticles of oxides and metals were focused on the stabilization of metallic or oxide nanoparticles in suspensions with not much concern about the control of crystal size and size monodispersity. For instance, Liu *et al.* [14] has reported an increase in thermal conductivity of up to 23.8% with respect to fluid base, using 0.1% v/v copper nanoparticles in water. The nanoparticles were polydisperse and their size varied between 50 and 100 nm.

An additional advantage of using nanofluids is the minimum risk of obstructing, eroding or corroding the conducting lines in cooling systems because of the expected low volume fractions of the nanoparticles and their nanometric size (far below 100nm). On a phenomenological basis, there is a lack of an explanatory model for the observed increase in the thermal properties of the nanofluids with respect to base fluid. Available models

underestimate the thermal conductivity when predicted values are contrasted with experimental results. Accordingly, there is a need for more precise experimental data obtained from nanofluids prepared with a precise control of its characteristics to feed the models and verify the theoretical expectations [14, 15].

Based on the above considerations, the present research addresses the development and optimization of a copper-bearing nanofluid with a precise control on composition, size and size monodispersity of the dispersed phase. Copper has been selected as the most promising material since this material combines the characteristics of a high thermal conductivity with relatively low cost and simplicity of synthesis. More specifically, the synthesis of copper nanoparticles with suitable size and size distribution, their stabilization in ethylene glycol and the determination of the nanofluids thermal conductivity will be attempted. Copper nanoparticles will be synthesized by reduction of copper ions by using reducing agents in solution phase (aqueous or non-aqueous). Synthesis conditions will be optimized to achieve a fine tuning of nanoparticles size. The selection of the synthesis method is based on environmental considerations and expected yields large enough to prepare the corresponding nanofluids. The nanoparticles and nanofluid will be structurally (XRD), morphologically (SEM, TEM), and thermally (thermal conductivity) characterized as a function of the size and concentration of nanoparticles in the base fluid (ethylene glycol).

1.2 Literature Review

Several reports have been published about the synthesis of nanoparticles including metals, non metals and polymers [16-21]. Emphasis has been focused on the synthesis of nanoparticles through solution routes due to their simplicity for scaling-up. Solution-based approaches are based on the reduction of metal ions by a reducing agent. In some cases the reducing agent is the solvent itself. The following section summarizes the results of our review of literature and is arranged from the nanocrystal synthesis and fluid preparation point of views.

1.2.1 Synthesis of copper nanoparticles by aqueous and non- aqueous routes.

Balogh and Tomalia [22] synthesized copper nanoparticles in Panam dendrimers as templates. In this case, the dendrimer acted as a nano-reactor providing ligand sites for the fixation of the copper ions. First, copper ions were complexed with surface modified poly(amidoamine), (PANAM); next, hydrazine is contacted with the complex metal solution to reduce the ions into the metallic state. Produced nanoparticles exhibited good stability in absence of oxygen. Although the size of nanoparticles was not determined, indirect optical measurements suggested sizes smaller than 2 nm.

Erchov [23], prepared 4-nm copper nanoparticles under the effect of γ -radiation and in presence of polyethyleneimine (PEI) and. The irradiation in aqueous systems produced hydrated electrons and free H^* and OH^* radicals. These radicals promoted the reduction of the copper ion. Qiu, Dong, et al [24], have synthesized spherical copper nanoparticles in

water/oil microemulsions using sodium dodecyl sulfate (SDS) as surfactant, isopentanol as co-surfactant, cyclohexane as oil phase and an aqueous solution of CuSO_4 . The reducing agent was sodium borohydride. The formation of copper was confirmed by XRD analyses. It was also found that the size and distribution of the copper nanoparticles were strongly dependent of molar ratio of water to surfactant, 'w'. For low 'w' values, the size of nanoparticles was between 3nm and 6nm. Larger 'w' values favored the production of larger particles with sizes between 24nm and 43 nm. The authors reported that an increment in copper concentration was conducive to an increment in the size distribution of synthesized nanoparticles.

Jana, et al [25], used a seed - mediated growth method to prepare cubic copper nanoparticles. The seeds were produced by reduction of copper ions by sodium borohydride. The diameter of nanoparticles was around 5 – 6 nanometers. In a second stage, copper seeds were added to a Copper aqueous solution followed by the drop-wise addition of ascorbic acid as a weak reductant agent. The copper seeds accelerated the reduction of copper ions by acting as pre-existing nuclei in solution. TEM images evidenced the formation of cubic-shaped particles with sizes between 75 and 250 nm. The size was dependent on the synthesis conditions. Ohde et al [27], used micro emulsions to control the size of copper and silver nanoparticles. The use of supercritical carbon dioxide, as a less expensive and environmental friendly route, was explored. The synthesis approach consisted in the formation of a copper aqueous emulsion in supercritical CO_2 . The reducing agent was added to this emulsion. The size of silver and copper nanoparticles varied between 5nm and 15nm. It was suggested that the

rapid expansion of supercritical solution lead to the agglomeration of particles. The authors suggested the use an amino functional group to minimize the inter-particle aggregation.

Aslam *et al.* [26], used the *Brust* synthesis route to synthesize copper nanoparticles. They used copper chloride as the precursor, sodium borohydride and three capping agents: 1-dodecanethiol, tridecylamine and lauric acid. The average size of the nanoparticles was around 5 nm in presence of dodecanethiol; 6.5 nm in tridecylamine and 10 nm when lauric acid was used. 1-dodecanethiol also helped to prevent the oxidation of the nanoparticles. Chen *et al* [29], used a modified Brust approach where a solution of copper sulfate was mixed with a solution of Cetyltrimethyl-ammonium bromide (CTAB). Decanethiol was added to this solution to form an emulsion that was contacted with sodium borohydride. After two hours of reaction, copper nanoparticles with sizes ranging from 1nm to 40nm were produced. The size of nanoparticles was strongly influenced by the CTAB concentration.

Wu and coworkers, [28], synthesized copper using ascorbic acid as reducer and antioxidant in the presence of PVP, the stabilizing agent in water. The nanoparticles size was between 2.4nm and 4.4nm. XRD analyzes verified the FCC structure of the copper particles. Song *et al* [30], used a transfer-phase method where a solution of copper sulfate was mixed with an organic solution of bis(ethylhexyl)Hydrogen Phosphate, (HDEHP), in n-heptane. Copper ions were complexed with DEHP⁻ species and transferred from the aqueous to the organic solutions. The organic solvent was separated and contacted with the sodium borohydride

solution. XRD showed the peaks corresponding to metallic copper. TEM images evidenced the formation of polydisperse nanoparticles averaging 60nm of diameter.

Sun et al, [59], synthesized copper nanoparticles using ethylene glycol as reducing agent. The reaction was improved by adding sodium hydroxide. The solid was recovered at different stages of the reaction that allowed verification of the precipitation of Cu_2O prior to elemental copper precipitation. The Cu particles presented a size near to 100 micrometers and were cubic in shape. The formation of sodium sulfate which co-existed with elemental Cu represented a problem for the preparation of any nanofluid by using this approach. Park et al [53], synthesized copper nanoparticles in diethyleneglycol media. They showed that variation in addition of stabilizing agents (Poly-N-vinylpyrrolidone), temperature and flow rate of copper salt solution affected the size and shape of final copper nanoparticles. They also recommended the use of Sodium phosphi-monohydrate - $\text{NaH}_2\text{PO}_2\cdot\text{H}_2\text{O}$ as co-reducing agent. The amount and flow control of this later compound allowed a kinetic control of the reaction. The size of copper nanoparticles ranged between 45nm and 53nm.

1.2.2 Nanofluids preparation

Although the synthesis of copper particles from solutions is somehow well documented, there is a lack of systematic studies on the size-controlled synthesis of copper-bearing nanofluids. It can be attributed to the fact that most of the synthesis routes do not provide high yields, good control of nanocrystal size or poor chemical stability of copper nanoparticles.

Liu *et al* [14], measured the thermal conductivity of Cu-bearing nanofluids using the hot wire technique. Copper acetate was used as the precursor salt whereas hydrazine was selected as the reducing agent. The use of an inert atmosphere was necessary along with a precise control of temperature. Particles were strongly aggregated and exhibited different shapes. The thermal conductivity values were not reproducible at all and a change of thermal conductivity with time was observed; after certain time, the conductivity of the system became similar to the fluid base. This work did not discuss how stable the suspension was; however, the strong aggregation between particles could have influenced thermal conductivity. Moreover, the drop in thermal conductivity with time could have been attributed to the aggregation and settling of the nanoparticles in the fluid.

Huang *et al* [31] designed and constructed a new device for the determination of the thermal conductivity in nanofluids. The synthesis procedure considered copper particles dispersed in ethylene glycol in absence of surfactants. Nanoparticles averaging 120 nm in diameter were synthesized in an electric arc system and then collected and dispersed in the cooling fluid. In order to prevent the particle agglomeration fresh nanofluid had to be added into the measurement system.

Eastman *et al.* prepared various nanofluids in water and ethylene glycol [32]. Copper oxide, CuO, and alumina, Al₂O₃, synthesized by using a vapor condensation method, were used to prepare water-base fluids. In a second approach, a 10-nm copper-ethylene glycol nanofluid

was prepared using a modification of the VEROS technique (vacuum evaporation onto a running oil substrate). The thermal conductivity of prepared nanofluids was determined by using the transient hot-wire technique. The results verified the strong relationship between the thermal conductivity of the nanofluid, nanoparticle size and the corresponding thermal conductivities of both, the metallic disperse phase and the base fluid.

1.2.3 Nanofluids and thermal conductivity of suspensions

The increase in thermal conductivity in cooling systems has been extensively reported for aqueous and not aqueous media as well as conductive and non conductive nanoparticles. Liu *et al.* [14], found an increase of 23.8% in aqueous nanofluid thermal conductivity increase with respect to base using 0.01 Cu volume fraction. The nanoparticles were polydisperse and their size varied between 50 and 100 nm, Eastman *et al.* [66], found an increase close to 40% in copper in ethylene glycol nanofluid thermal conductivity, when the volumetric concentration for copper nanoparticles with average size of 10 nm was of 0.3vol %. D-H Yoo *et al.* prepared TiO₂, Al₂O₃ based water nanofluids and WO₃ and Fe in ethylene glycol [67]. The average particle size was estimated as 25nm (TiO₂), 48nm (Al₂O₃), 10nm (Fe) and 38nm for WO₃. They evaluated a volumetric load of the nanoparticles in the 0.005-1.00 % range. The nanofluid reached a 12% increment in its thermal conductivity when 0.3 v/v % of WO₃ was used. The same increase was obtained for TiO₂ nanofluid with a volumetric fraction of 0.5% whereas the presence of Fe nanoparticles caused an enhancement of 16% in the thermal conductivity. A weak increase in the thermal conductivity was attained in the case of alumina nanoparticles (2% at 0.5 volume fraction). As observed, the metal bearing nanofluid exhibited the larger increase of thermal conductivity. However, it was not possible

determine their size-dependence on thermal conductivity due to difference in average particle size and composition for the nanofluids which were evaluated.

Based on the described above information, the increase in thermal conductivity can be achieved by suspending a proper amount of suitable nanoparticles; nevertheless, the precise effects of materials (structure, composition, size, volumetric load, shape) and solvent properties on the mechanisms involved with the enhancement of thermal conductivity is still unclear. Accordingly, the present work addresses the determination of the suitable conditions for copper nanoparticle synthesis and the preparation of the corresponding nanofluids. Moreover, this work also developed an improved version of a transient hot wire apparatus for thermal conductivity measurements in fluids in a reliable and reproducible manner.

2 THEORETICAL BACKGROUND

2.1 Nucleation and growth of nanoparticles

Nucleation and growth are complex processes that are involved with the formation of a solid phase within a solution media. In our syntheses' approaches, the nucleation process starts only after dissolution of a precursor oxide. Released species in solution are then reduced by hydrazine (in water) or ethylene glycol (in polyol media) to give the final solid phases. In the reduction of Cu (II) species, Cu_2O is considered an intermediate phase [28, 34, 51]. This intermediate must be fully dissolved prior to the final reduction of Cu(I) species into metallic Cu. Once metallic Cu particles are formed, they tend to form clusters (early nuclei) or start growing by aggregation of single crystallites, incorporation of reduced metal from the solution, or by further growing at the expense of the dissolution of small particles through the so-called Ostwald ripening process [33].

The key to form non-aggregated nanoparticles is a fast nucleation followed by a relative slow and short growth stage. LaMer's diagram, shown in figure 1, is very useful to describe the most important aspects for monodisperse nanoparticles synthesis. According to this diagram, a burst nucleation will take place when actual concentration of metallic species is above a critical concentration, called *saturation concentration*. This burst nucleation stage involves a very fast nucleus formation after an episode of apparently chemical inactivity. During this stage there is an increase in nucleus number and a simultaneous drop in metal concentration (consumption of solute species) until the concentration of dissolved species falls below the critical concentration. At the end of this stage, no more nuclei appear. Formed metallic nuclei

will start to grow until they reach an equilibrium condition in the subsequent growth stage [33, 52, 53]

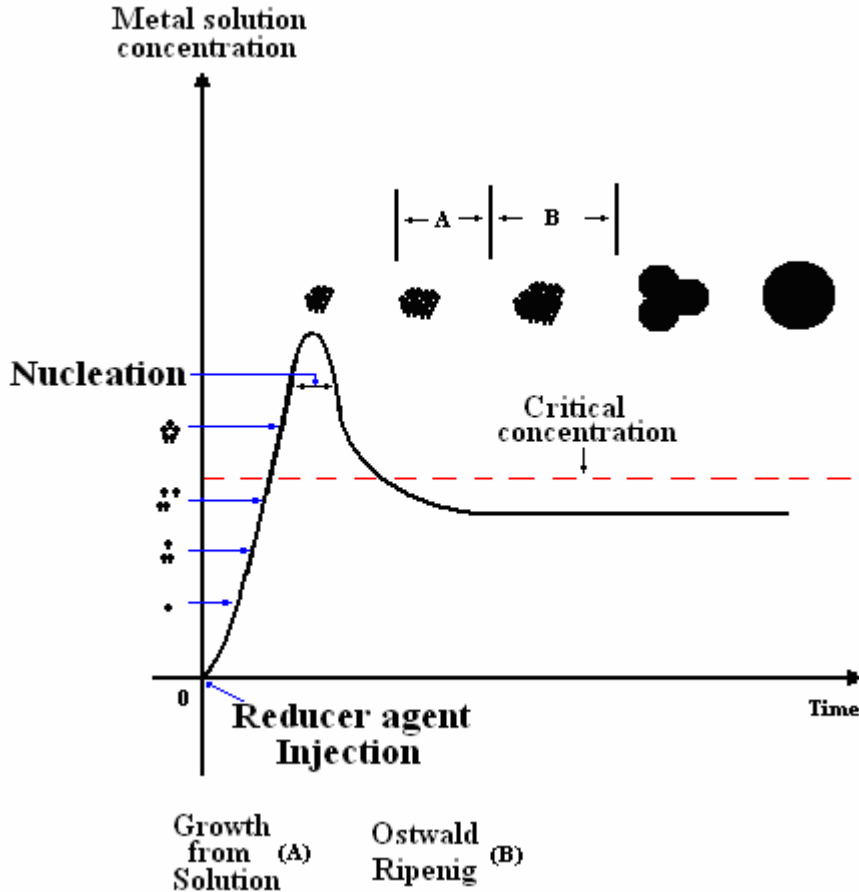


Figure 1: LaMer's model for the synthesis of monodisperse nanoparticles [52].

2.2 Prevention from aggregation of particles

As discussed above, once nuclei are formed they can also aggregate in order to decrease the total surface energy. This aggregation, which can be a consequence of attractive Van der Waals forces between crystals, should be inhibited or limited to restrict the final particle size at the nanometric scale. There are two strategies to prevent nanoparticles from aggregation: the first involves the use of substances that lead to steric repulsion between individuals.

Polymers or surfactants are examples of this type of growth and/or aggregation inhibitors. The second option consists in providing the nanoparticles surface with a net charge to promote electrostatic repulsive forces among them. It can be achieved by adsorbing charged species (hydroxyl or acetate species, for instance) onto nanoparticles surface [33, 54].

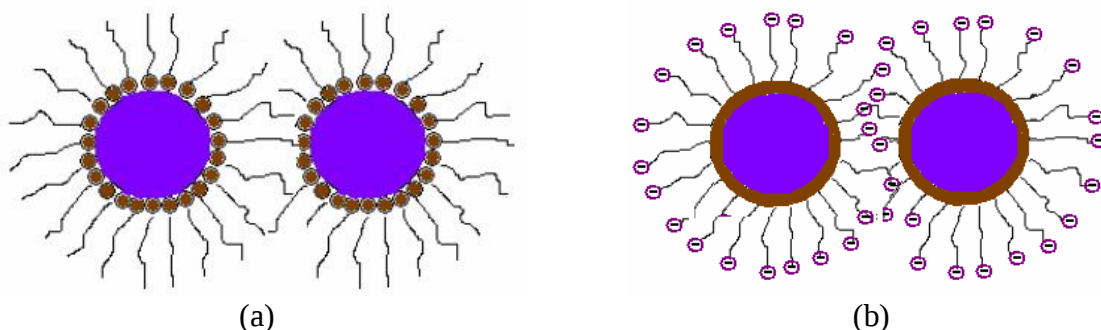


Figure 2: surface agent to prevent agglomeration, (a) Steric repulsion, (b) electrostatic repulsion

Surfactants have polar groups capable of bonding to nanoparticle surface and are sufficiently big to confer a physical impediment to nanoparticle coalescence. Surfactants are compounds with amphiphilic characteristics, i.e. they exhibit hydrophilic or hydrophobic properties [33, 55, 56]. Figure 3 shows the linear structure of two common surfactants cetyltrimethylammonium bromide (CTAB), and sodium-dodecylsulfate (SDS) [33].

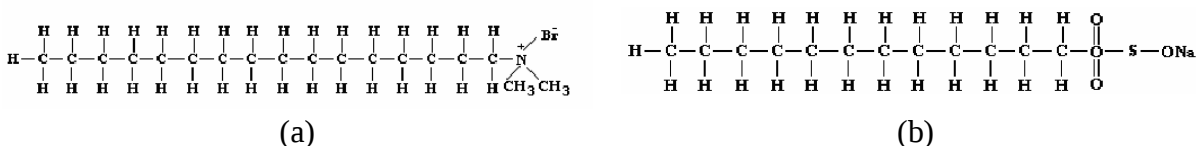


Figure 3: Two common surfactants, (a) Cetyl trimethylammonium bromide surfactant, (b) Sodium dodecyl sulfate

On the other hand, organic compounds with an electron-pair donor atom (such oxygen or nitrogen), are capable of forming strong bonds with nanoparticle surface. The energy of this binding is higher than for surfactant molecules. Figure 4 shows the structure for

polyvinylpyrrolidone, a soluble polymer and well-known ‘capping agent’ that corresponds to the previous description [33, 54].

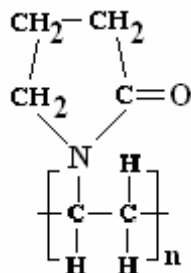


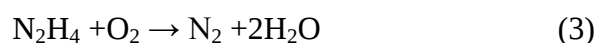
Figure 4: Polyvinylpyrrolidone (PVP) structure

2.3 Hydrazine reduction properties

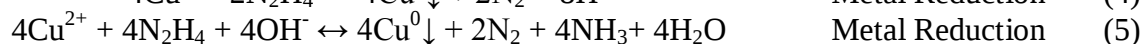
The reduction of copper, and certain metals, by hydrazine can be explained by the following redox reactions [33, 34].



Special care must be taken regarding hydrazine contact with oxygen since it promotes degradation [34]:



Where the reactions involved in the process of metal reduction are the next set of mechanisms:



For copper it is possible establish the half cell potential as follows [71]:

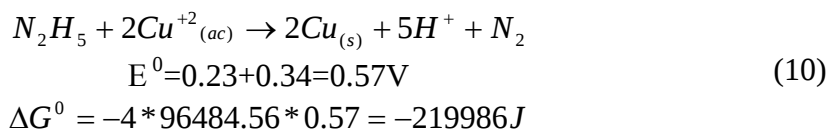




The variation in the Gibb's free energy for the reduction of Cu by hydrazine can be determined by using the following relationship.

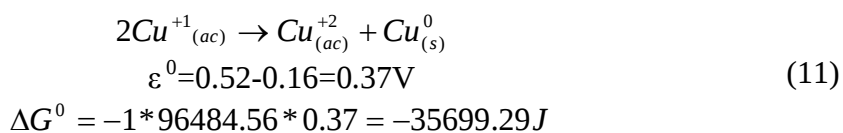
$$\Delta G = -nf\varepsilon \quad (9)$$

In equation 9, 'n' corresponds to the number of electrons in the balanced equation, and F is the Faraday constant (96484.56J/mol*V). We started calculating the Gibb's free energy for reaction described in equation 10:



The negative value of the standard Gibb's free energy suggests the viability of the reduction of Cu(II) species according to reaction described in equation 16. However, it must be emphasized that a positive value in the Gibb's free energy could be related to the formation of quite stable intermediate phases that will completely inhibit the formation of elemental copper.

Another reaction can also take place.



The free energy value for equation 11 suggests that this reaction can also take place.

In all cases evaluated above for Gibb's free energy, lead to that each reaction can take place, the fact of which reaction will be occur, is a kinetic problem and is necessary experimental data for establish the reactions evolution.

2.4 Polyol process fundamentals

2.4.1 Introduction

The use of high boiling point alcohols permits the attainment of reach suitable conditions for reduction of metal ions, such as noble Au, Ag, Pt and more electropositive metals such as copper, cobalt, nickel, and iron, to their zero valence state. The reduction in alcohols has another important characteristic: the de-hydrating property of the alcohols that will help prevent the oxidation of metal nanoparticles [57].

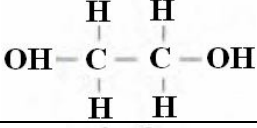
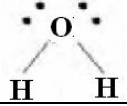
Metal reduction in alcohols, especially in those having many OH groups, is referred to as the polyol process. This process has been used for synthesis of metal powder in the range of micron and submicron size. In general, the alcohol acts as solvent and reducing agent. In order to achieve a suitable rate of reduction a soluble salt of the metal to be synthesized is added to the polyol and heated at a prescribed temperature or under boiling polyol conditions [53, 57-59].

2.4.2 Polyol properties

Due to the presence of hydroxyl groups the polyol, in the same way as water, can act as solvent for many substances with a net dipolar moment or with polar groups (solvation process). This characteristic of polyols can be represented by their dielectric constant,

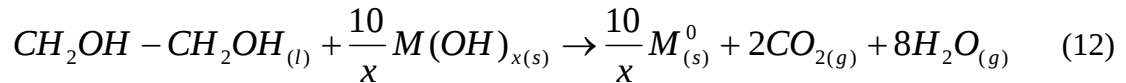
(permittivity in a more general concept). Table 1 shows the relative permittivity for ethylene glycol (EG) and water.

Table 1: Ethylene glycol and water properties [62]

Liquid base	Molecular weight, g/mol	Molecular formula	Molecular structure	Boiling point at 1 atmosphere (°C)	Density (g/cm ³)	Relative permittivity
Ethylene glycol	62.07	C ₂ H ₆ O ₂		194.8	1.115	40
Water	18.02	H ₂ O		100	1.000	78.5

2.4.3 Thermodynamics of polyol process

It is assumed that the process of reduction of metal is due to a complete oxidation of ethylene glycol (EG) and the precursors are oxide and hydroxides of the metal to be reduced, it is possible to make a thermodynamic analysis of the equilibrium conditions in the redox process at the boiling point. Under such conditions the overall reaction can be written as [57]:



The assumption of complete oxidation considers only the best condition for reducing the metal ions that is the transformation of EG in H₂O and CO₂ by combination with oxygen or hydroxyl groups from precursors. Under this consideration the Gibb's free energy is the summation energy of formation of CO₂, H₂O and zero valence metal minus the energy of formation of precursors M(OH)_x and EG [57, 59].

$$\Delta G_{red} = 2\Delta G_f(CO_2) + 8\Delta G_f(H_2O) - \frac{10}{x}\Delta G_f(M(OH_x)) - \Delta G_f(EG) \quad (13)$$

In a real case scenario the formation of intermediate solid phases is common; in the particular case of copper reduction, the formation of Cu₂O has been confirmed as well as Cu-based alcoxide. These intermediates will be dissolved by EG prior to the final reduction into metal. This kind of multi – step reaction has a strong impact in reaction kinetics and hence, on the nanoparticle size and shape.

Figure 5 shows the Gibb's free energy required for the reduction of some metals. It was calculated by using equation (2) that does not consider the formation of any intermediate phase. Figure 5 shows the precursor compound instead of reduced metals because the nature of this precursor affects the overall reduction process. The vertical lines correspond to expected free energy variation based on data found in the literature for the free energy of formation for substances involved in the reaction. The dark labels are assigned to metal oxides that can not reduce to zero valence metals in ethylene glycol under boiling conditions.

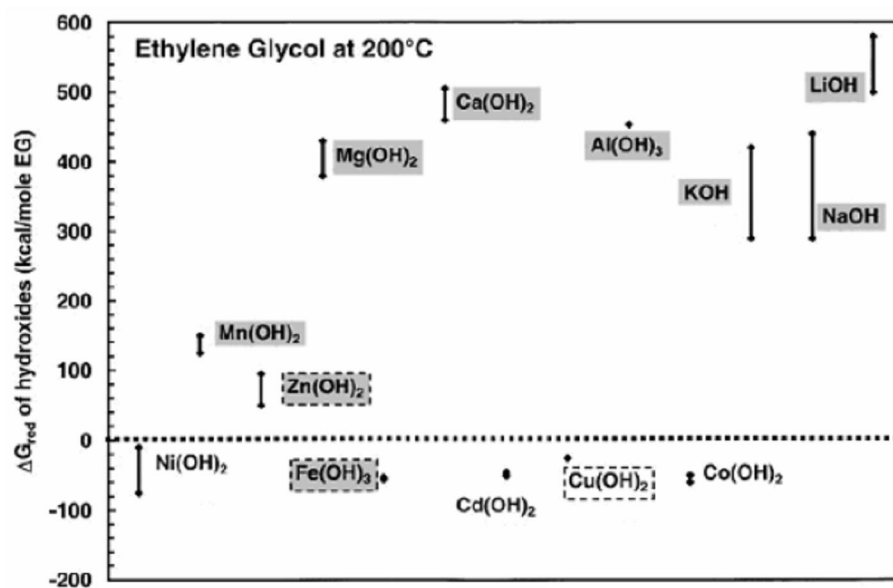
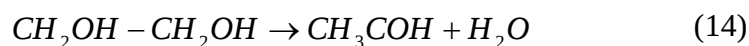


Figure 5: Calculated ΔG of reduction for some hydroxides using ethylene glycol as solvent and reducing agent at a temperature of 200 Celsius degrees. A complete oxidation of the reducing agent is assumed. [57]

In the Cu-ethylene glycol system, the formation of complex compounds and intermediate cuprous oxide [59] is likely to occur. Ethylene glycol will partially transform into aldehyde and, in later stages, gets converted into biacetyl by oxidizing processes [57, 59] involved with the copper reduction to the zero valence state. Considering the information provided in literature, [53, 57-59], it is possible to suggest that some of probable reactions that take place in copper reduction by ethylene glycol are given in equations 14-16:

Ethylene glycol to acetaldehyde:



Copper intermediate compound to cuprous oxide:



Reduction of copper (I) to zero valence state:



When NaOH is added to ethylene glycol the $\text{CH}_3\text{COCOCH}_3$ conversion to acetaldehyde is expected to be promoted. This compound participates in the last stage of Cu reduction[59].



Therefore, based on the information available in the literature as well on our own experimental data, the reduction of copper in polyol process through a multi-step process can be suggested [53, 57-59]. Figure 6 summarizes the progress of the steps involved with the formation of elemental Cu in EG solutions.

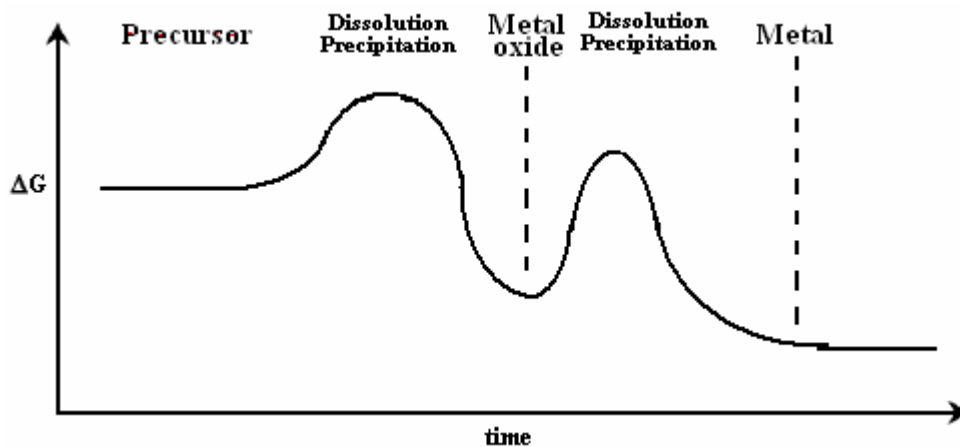


Figure 6: Reaction steps and intermediate phases expected in polyol process using ethylene glycol as reducing agent for non zero valence metal, based on the information and data in references 53, 57-59.

2.5 Fundamentals of materials characterization techniques

2.5.1 X-Ray diffraction (XRD)

XRD permits the identification of crystalline structures in samples. The analysis of the patterns can lead to the determination of other structural parameters such as strain state, crystallite size, phase composition and preferential growth of the crystals. In XRD, a filtered X-ray beam is directed on the sample and the beam is diffracted when it interact with a plane in the crystalline structure, for detect diffracted beams signal of different planes, is necessary that the diffracted beam are in phase with respect to another one, in other case the beams cancel [60-62].

Figure 7 shows the basic aspects involved with a diffraction experiment. The interplanar distance 'd' can be calculated using Bragg's equation and the average crystallite size by using Scherrer's equation (table 2). An approximate demonstration for the last can be found in [62].

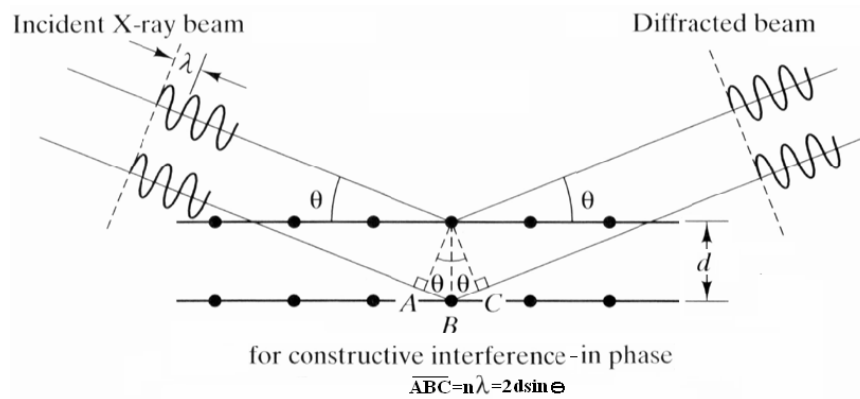


Figure 7: Basic principles of a usual x-ray diffraction experiment.

$$n\lambda = 2d \sin(\theta) \quad (18)$$

$$t = \frac{0.95\lambda}{B \cos \theta_m} \quad (19)$$

Equation 18 is the so-called Bragg's equation for inter planar distance calculation whereas equation 19 is the Scherrer's relationship used for crystallite size calculations. λ is the wavelength of the x-ray beam, d correspond to inter planar space, θ is the diffraction angle and 'n' is a integer number relationship with the constructive interference for the x ray beams travel at different pats, 'B' is the width in radians of the diffraction peak at half of the highest intensity.

Lattice parameter calculation

Equation 20 present the relationship between the interplanar spacing', plane indexes and crystal lattice parameter 'a', for cubic systems.

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad (20)$$

In this work a the XRD analyses were carried out in a Siemens D 500 powder X-Ray diffractometer (Engineering Science and Materials Department, University of Puerto Rico, Mayaguez campus), with Cu-K α source and β -Ni filter. All the scans were recorded in the 2θ range from 40° to 80° degrees; the scan rate was 0.03° per second.

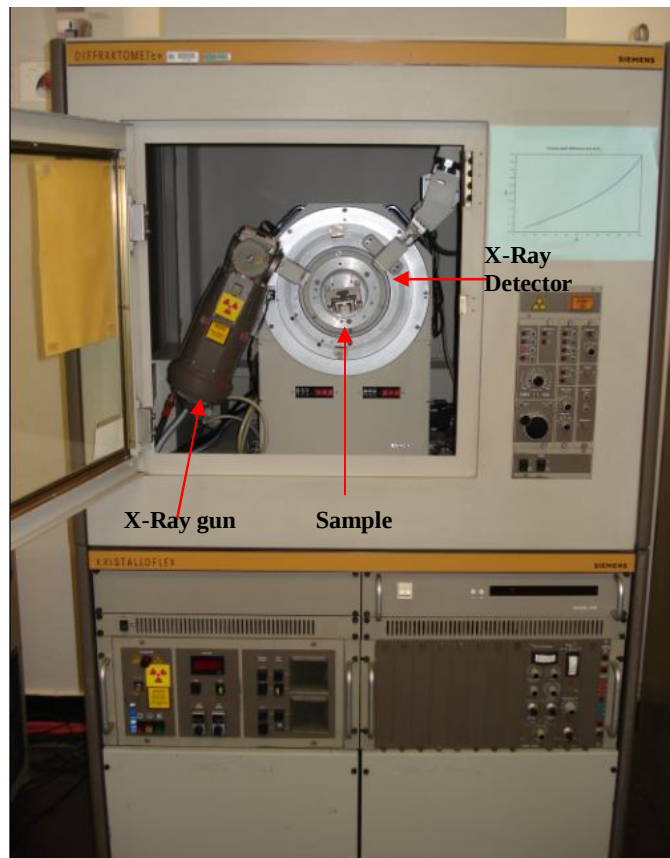


Figure 8: Siemens D 500 powder X-Ray diffractometer, Engineering Science and Materials Department, University of Puerto Rico, Mayaguez campus.

2.5.2 Scanning Electron Microscopy (SEM)

In SEM, a filtered high energy electron beam is directed to a sample that requires having an electrically conductive surface. After striking the surface a variety of signals are produced including secondary electrons, back scattered electrons, characteristic x-rays, light, transmitted electrons and specimen current. Using a special detector the secondary electron signal can be used to build a surface image; for this purpose, the sample surface is scanned point by point to create the image of the investigated portion of sample surface.

In our case, the images were recorded in a JEOL - JSM-5410 LV Scanning Electron Microscopy and was used to obtain information concerning to powder morphology and particle size [60, 62].

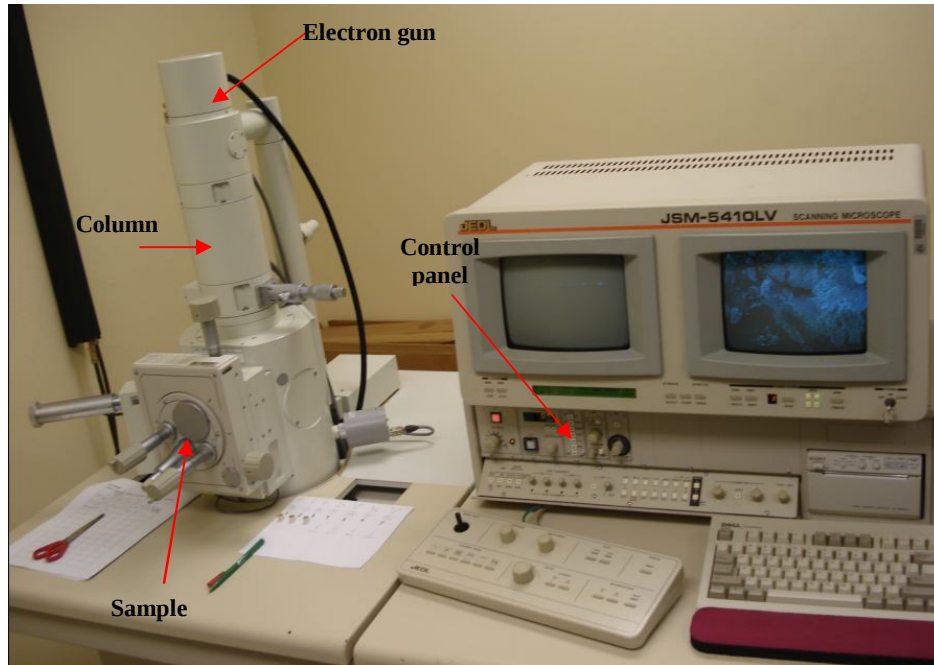


Figure 9: Scanning Electron Microscope in Biology Department, Puerto Rican university, Mayaguez campus.

2.5.3 TEM - Transmission Electron Microscopy

In a TEM microscope, an electron beam is emitted in microscope top column, the electron beam travel trough the column in high a vacuum and by mean of electromagnetic coils the beam is be positioning and focus to obtain a very thin beam. This beam hits the sample and depending on the energy and sample density, some electrons pass through the sample and magnifier lens and strike a fluorescent screen below to sample.

The energy with that the beam strike the screen is relative to the path follow for the beam, and with the energy lost when beam interact with sample, this differences in intensity energy for different positions produce on the screen a shadow image were is possible relate the sample borders, the thickness and density in sample with differences in darkness, as rule darker zones imply that only a few electrons was transmitted and lighter zones imply than many electrons crossing the sample, the image formed in the fluorescent screen is converted and pass to a monitor and can be directly analyzed by user or recorder [61, 62]. Same than in a SEM, interaction between sample and beam produce a various kind of signal such a secondary and backscattered electron that can be analyzed by mean of EDS, EELS and EXELFS to provide materials characterization

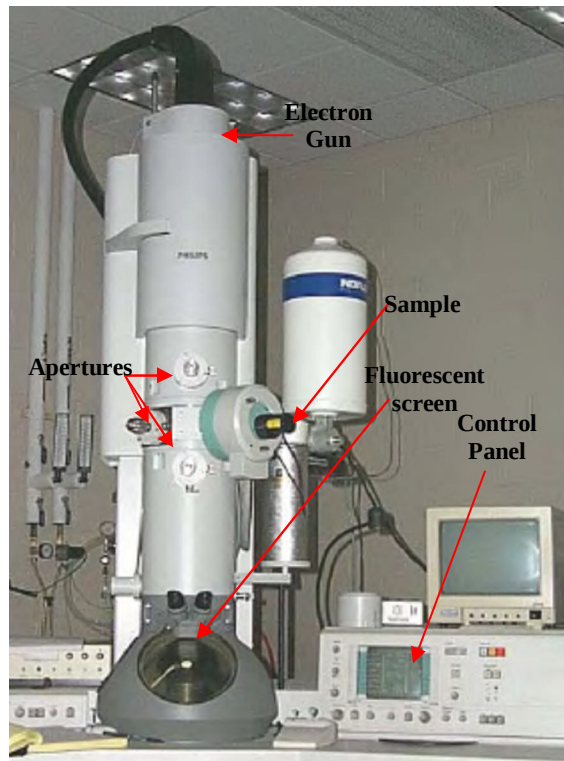


Figure 10: Philips CM200 UT transmission electron microscope, Materials Science and Engineering Department - Wisconsin University.

2.5.4 Ultraviolet – visible Spectroscopy (UV-vis)

When ultra violet or visible light is absorbed for a sample, electronic excitation is promoted. The excited species went back to their original state through a relaxation process, in which the energy can be transformed in heat or light. If the absorbed energy is sufficiently high new substances could be formed. In this process, the life of excited species is very short that explains the negligible increase in temperature.

UV-Vis spectrum is presented as the variation of optical absorbance with frequency (or wavelength number). If the power of light is known before, (P_0), and after passing through the sample (P), the transmittance, 'T', can be related to

$$T = \frac{P}{P_0} \quad (21)$$

And the percentage of transmittance is

$$T = \frac{P}{P_0} * 100 \quad (22)$$

The absorbance corresponds to the negative of the logarithm of transmittance. It is necessary to indicate that absorbance increases when the transmittance decreases.

$$A = -\log(T) = \log\left(\frac{P_0}{P}\right) \quad (23)$$

The absorbance 'A' can be calculated for a monochromatic radiation through the Beer's law:

$$A = \epsilon \cdot b \cdot c \quad (24)$$

Beer's law states that the absorbance is directly proportional to optical path and sample concentration, the constant of proportionality is called the molar absorptive coefficient (ϵ).

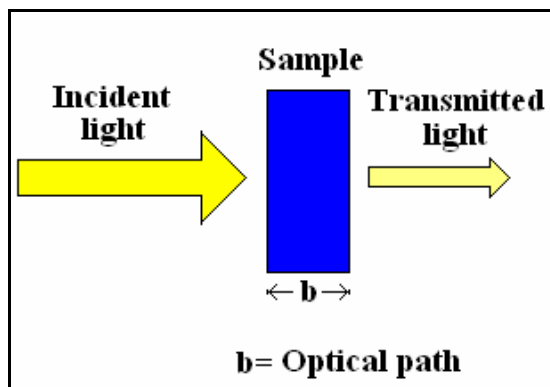


Figure 11: Decrease in transmitted ray due to absorbed radiation.

Metals such as gold, silver and copper present a strong absorption band attributed to a collective electron oscillation caused by an incident electromagnetic radiation. To understand the above described interaction, let us consider a metal as a cloud of electrons that move around a lattice ions structure. The interaction between an external electric field and electrons will lead to a dipole formation by means of the development of a surface polarization charge that in turn will produce a restoration force that opposes to electron displacement; in other words, the conductive electrons and external field interaction should lead to longitudinal oscillation of electron clouds, (plasma oscillation). Then, a plasmon corresponds to a quantum of energy for the collective cloud electron oscillation (figure 11). The plasmon peak position is affected by nanoparticles size and agglomeration level [52].

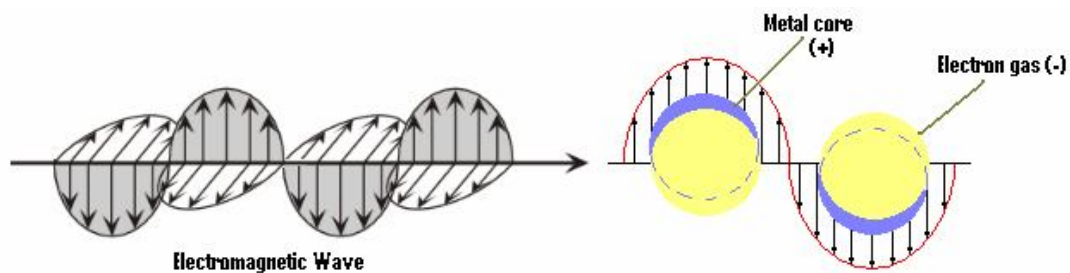


Figure 12. Metal electron cloud oscillation as consequence of interaction between electrons and external electromagnetic field.

For spherical copper nanoparticles the plasmon is expected in the region near to 590nm for nanoparticles bigger than 2 – 4 nm whereas for smaller sizes (clusters) it would be centered at around 300 nm [22, 63]. It must be remarked that the shape of nanoparticles can contribute to shift the plasmon peak [27, 25, 28, 64].

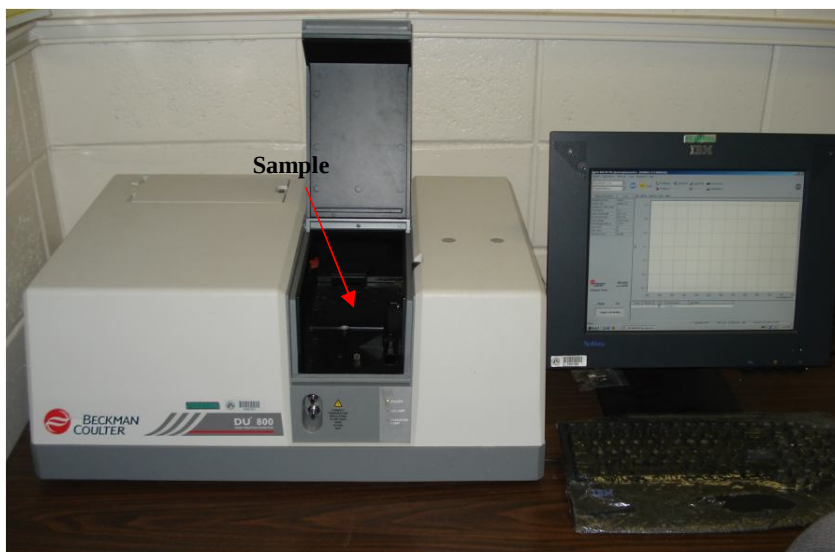


Figure 13: Beckman Coulter DU 800 UV/Visible Spectrophotometer, NANOMaterials Processing Lab – Engineering Science and Materials Department, University of Puerto Rico, Mayaguez campus.

2.6 Thermal conductivity measurements

In heat conduction, the heat flow inside a material without mass transport. Experimentally it is possible to show that the heat velocity per unit area, the rate in which heat energy is transferred of a point to other point in a homogeneous material, is proportional to temperature gradient inside material. In the most simple one-dimensional problem, this expression can be written as $q = \kappa * A * dt/dx$, where 'A' is the normal area to heat flow, and κ is a proportionality constant called thermal conductivity. 'k' can be used to characterize the materials; the larger the 'k' value the more conductive the material will be.

2.6.1 Thermal conductivity in fluid mixtures: Classical models

There are some semi-empirical formulas to calculate the thermal conductivity of binary mixture based in continuum formulation. So far, there is no model available to predict nanofluid thermal conductivity. The most well-known model is represented by Maxwell's relationship in equation 25. In this equation, ' k_p ' is the particle thermal conductivity, ' k_b ' the fluid thermal conductivity and ϕ is the particle volume fraction. Maxwell's equation can be used with adequate approximation in low concentration, micron-size particles. This model fails at high concentrations and in nanofluids [35, 39, 40].

$$k_{eff} = \frac{k_p + 2k_b + 2(k_p - k_b)\phi}{k_p + 2k_b - (k_p - k_b)\phi} k_b \quad (25)$$

A more sophisticated model that also fails when applied to nanofluids, although it is still adequate for low and high concentration suspensions of micron particles, is Bruggeman's

relationship presented in equation 26. This model assumes arbitrarily dispersed spherical particles [35, 40].

$$\phi \left(\frac{k_p - k_{eff}}{k_p + 2k_{eff}} \right) + (1 - \phi) \left(\frac{k_b - k_{eff}}{k_b + 2k_{eff}} \right) = 0 \quad (26)$$

Hamilton and Crosser presented a model that takes in account the particle shape. When the particle conductivity is greater than one hundred times the fluid conductivity the Hamilton and Crosser model takes the form of equation 27, [35, 39-42], where ‘n’ is an empirical number and is equivalent to $n = 3/\psi$, where ψ is the ratio between the area and volume of a sphere with equivalent particle volume. Maxwell’s model can be considered as an especial case of Hamilton and Crosser model where $\psi=1$,

$$k_{eff} = \frac{k_p + (n-1)k_b - (n-1)(k_b - k_p)\phi}{k_p + (n-1)k_b + (k_b - k_p)\phi} k_b \quad (27)$$

The above presented models presume diffusive heat transport and, with exception of the Hamilton and Crosser model, only take into account the thermal conductivity of particle and fluid. These models under predict the nanofluid thermal conductivity and create the necessity of developing new and more complete models capable to explain the experimental results for thermal conductivity in nanofluids. [35, 39-42]

Several works have been focused in introducing the effect of fluid particle interactions, ignored in early thermal conductivity estimations, such as nanoparticle Brownian movement,

nanoparticle clustering effects, liquid layering on the nanoparticle surface and the effect of size in phonon diffusion or the effect of the surface charge [35, 40-42]. We will discuss each one of these additional factors that can also affect the thermal conductivity in nanofluids, as follows.

2.6.2 Brownian motion

Liquid molecules can exert an unbalanced force over the nanoparticles, that could produce nanoparticle motion, if the nanoparticles can collide the heat interchange is facilitate and an increase in thermal conductivity will be expected. Experimental measurement shows that thermal energy transport due Brownian motion itself is too small with respect to liquid conduction heat energy transport, [31, 35, 39, 40, 43]; but is possible that its effects can contribute to thermal conductivity enhancement [44].

2.6.3 Nanoparticle clustering effects

Clusters exhibit a grid structure that confers a higher heat transport and enhancing thermal conductivity. A cluster is defined by the ratio between the volumes of a particle inside cluster to the cluster volume; when the ratio decreases the thermal conductivity increases. The limit case occurs when the nanoparticles are separated for a thin liquid layer. If the particle is sufficiently small, the increase in thermal conductivity is considerable and will can be explained by the ballistic phonon transport mechanism [35, 39, 40, 45].

2.6.4 Liquid layering on the nanoparticle surface

Liquid in the nanoparticle surface can present a more ordered structure than liquid in bulk. This ordering can be conducive to an increase in thermal conductivity in the same way as crystalline solids having higher thermal conductivity than liquids. Since ordered liquid layer is a surface phenomena, the increase in the region of the ordered liquid on the nanoparticle surface should have a significant effect on heat transport and hence, on thermal conductivity [31, 35, 46, 47].

2.6.5 The effect of size in phonon diffusion

In crystalline solids the heat transport is explained through the lattice vibration called phonon. Keblinski *et al* [48] have shown that it is not possible to use a macroscopic theory to give a description of heat transport phenomena in nanoparticles due to fact that in nanoparticles the crystal size is too small for phonon propagation, in other words, classical model, (diffusive heat transport), cannot be used to explain heat transport in nanoparticles, [35, 48, 49]. Keblinski *et al* [48], proposed a ballistically phonon movement across to nanoparticle to explain heat transport in such cases.

2.6.6 Effect of the surface charges

The addition of stabilizing agents during nanofluids preparation can also promote the ordering of the liquid on the nanoparticle surface. This ordering would provide ways in which heat transport is facilitated. Xue *et al.* [35, 50] through molecular dynamic simulation showed that resistance to phonon transport decreased when the interfacial bonding was

increased. In this way, if the solvent and nanoparticle conditions permit the development of a surface charge, an increment in thermal conductivity could be expected. In fact, charged specie on the nanoparticle surface would exert a pull-on effect over opposite charges in solution. The net effect will be the generation of ordered layers of charged species in solution surrounding the nanoparticle surface and then an increase in nanostructures volume fraction is obtained.

2.7 Thermal conductivity measurement techniques

There are several techniques to measure thermal conductivity in liquids. Each technique has specific restrictions that limit its applicability.

2.7.1 The parallel plate method

In this technique the sample is placed between two plates with area ‘A’ separated by a small distance. The whole system is thermally insulated to minimize heat losses. A specific flux of heat is produced on one of the plates. The system is design to assure that the heat will flow from one plate to another, implying that the heat will flow through sample. Under this condition, the temperature difference between plates is recorded and thermal conductivity is calculated using Fourier’s law according to equation 28.

$$k = \frac{Qd}{A\Delta T} \quad (28)$$

To improve the accuracy of this method, it will be necessary to avoid convective heat transfer because it would affect the heat losses through plates and lengthen the time for an accurate measurement [35].

2.7.2 Transient hot wire technique

This method consists in applying a current to a long and thin platinum wire immersed in a fluid. The wire temperature increases because of its inherent resistance. Since the diameter is negligible with respect to the wire length, the temperature in the wire will be very close to the temperature in adjacent fluid. If no convective effect takes place, the increase in temperature in the fluid will be controlled by a thermal conductive process.

The temperature of the wire is determined by knowing the corresponding resistance. A voltage is applied to the wire ends and the temperature is determined from a calibration curve. This curve is obtained by determining the platinum wire resistance as function of temperature. To measure the resistance, an unbalanced Wheatston bridge is used to reduce impedance error [35-38]. The relation between thermal conductivity, temperature and time is given by equation 29, [35-38].

$$k = C \frac{q}{4\pi(T_2 - T_1)} \ln\left(\frac{t_2}{t_1}\right) \quad (29)$$

T_i corresponds to the temperature for time t_i , 'q' is the power dissipate, 'k' the thermal conductivity and 'C' a constant related to wire length and coating, if existent.

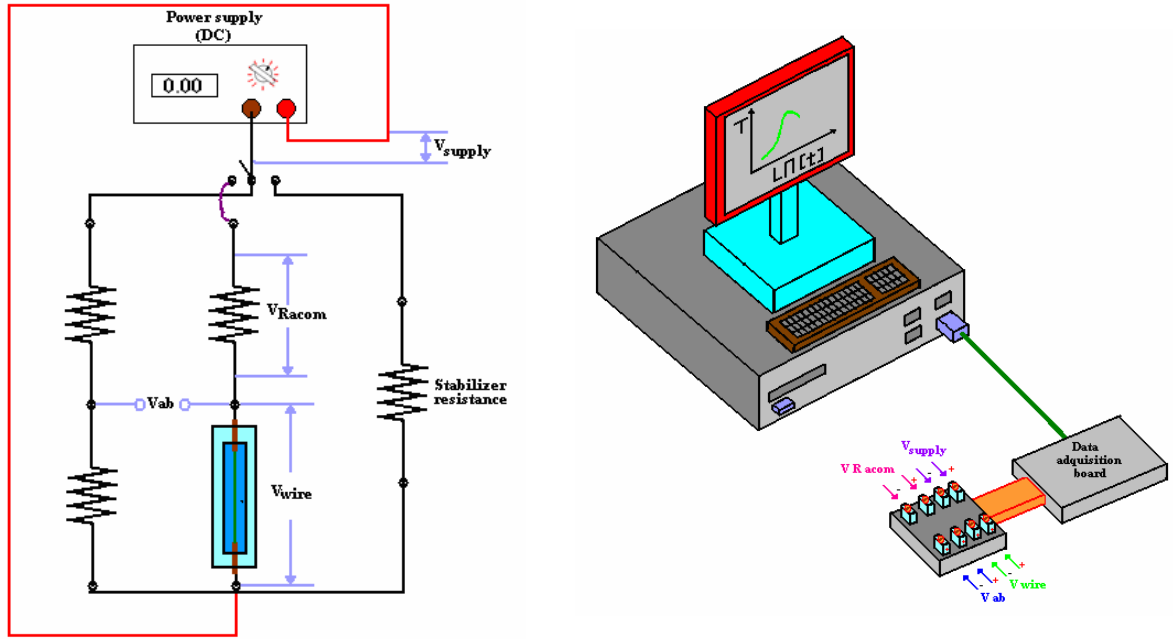


Figure 14: Schematic of a hot-wire system

Figure 12 shows the transient hot-wire apparatus. We use a $25\mu\text{m}$ diameter platinum wire coated with $1.5\mu\text{m}$ thickness of polyester enamel. The total diameter of the coated wire was $28\mu\text{m}$. The purpose of coating was to isolate the wire from fluid for make thermal conductivity measurements in electrical conductive fluids. Due to small coating thickness, the model presented in equation 29 does not vary substantially, [35], but it is necessary to conduct calibration measurements to determine the correct value for 'C' constant in equation 29, [35].

The transient hot wire approach is a fast and cheap technique to measure thermal conductivity in fluids. It has the advantage of requiring minimum sample preparation prior to measurement.

3 METHODOLOGY

3.1 Materials

All reagents were of analytical grade and were used without further purification. Required weights of Cu(II) sulfate pentahydrate salt, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, with 98.0 – 102.0 % in purity (Alfa Aesar) and Cu(II) acetate salt, $\text{Cu}(\text{CH}_3\text{CO}_2)_2$, (99%, Strem Chemicals), were dissolved in high purity water, (18M Ω) and ethylene glycol, respectively. Hydrazine, (N_2H_4), (+98%, Alfa Aesar), ethylene glycol, ($\text{HOCH}_2\text{CH}_2\text{OH}$), (99%, Alfa Aesar), were used as reductant agents in aqueous and non-aqueous media, respectively. Sodium dodecyl sulfate, (SDS), $\text{C}_{12}\text{H}_{25}\text{NaO}_4\text{S}$, 98% min, Fisher Scientific, Polivinylypyrrolidone, (PVP), $\text{C}_9\text{H}_9\text{NO}$, (Alfa Aesar), and Cetyl trimethyl ammonium bromide (CTAB), $\text{C}_{19}\text{H}_{42}\text{NBr}$, high purity grade, AMRESCO were used as the capping agents. Sodium hydroxide, NaOH (+98%, Sigma - Aldrich) was also used to accelerate the reduction reaction in ethylene glycol. Ethanol $\text{CH}_3\text{CH}_2\text{OH}$, (96 % Alfa Aesar) was used to wash and store the nanoparticles.

3.2 Synthesis of Copper Nanoparticles

The copper reduction was achieved by using two procedures. The first consisted in the reduction by hydrazine in aqueous solution; the second approach considered Cu formation in ethylene glycol solutions. Each reduction experiment was carried out in triplicate.

3.2.1 Aqueous reduction of Cu(II) ions

Required amounts of hydrazine and Cu(II) sulfate solutions were contacted with high purity water at room temperature conditions. Possible re-oxidation of Cu precipitates was avoided by conducting the reduction reaction in tightly closed reaction vessels. The appropriate contact between species was guaranteed by using a magnetic stirrer system (see figure 15). Figure 16 summarizes the synthesis procedure. At the end of the contact time, the suspension was treated by centrifugation. Recovered solids were washed twice and stored in ethanol. The effect of concentration of sodium hydroxide, cetiltrimethyl-ammonium borohydride (CTAB) and Sodium dodecylsulfate on the formation and average crystallite size of Cu particles was evaluated.

The concentrations of Copper sulfate, CTAB, SDS, NaOH and hydrazine used in their reduction experiments in this section are presented in Table 2. , and more important conditions used for enhance the nanoparticle synthesis are presented in table 3. The time of reduction is not presented but ranged between 4min to 34h.

Table 2: Concentration of chemicals used in this work for copper nanoparticles synthesis in water.

	A	B	C	D	
[M] CuSO ₄	0.016	0.032	0.048	0.064	E
[M] N ₂ H ₄	0.06	0.12	0.24	0.7	F
[M] SDS	0.00052	0.0026	0.0052	0.0104	G
[M] CTAb	0.00052	0.0026	0.0052	0.0104	H
[M] NaOH	0.016	0.16	0.8	0.0	I

Table 3: More representative aqueous synthesis conditions used in this work, (Based on table3)

Parameter unchanged	Parameter changed			
AF	AE	BE	CE	DE
AE	AF	BF	CF	DF
AF AE	AI	BI	CI	
AF AE	AG	BG	CG	DG
AF AE	AH	BH	CH	DH

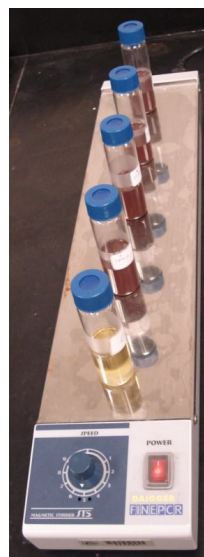
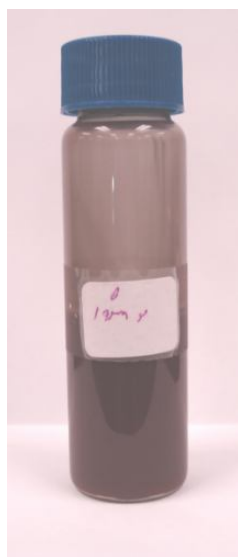


Figure 15. Stirrer used for Hydrazine synthesis experiments.

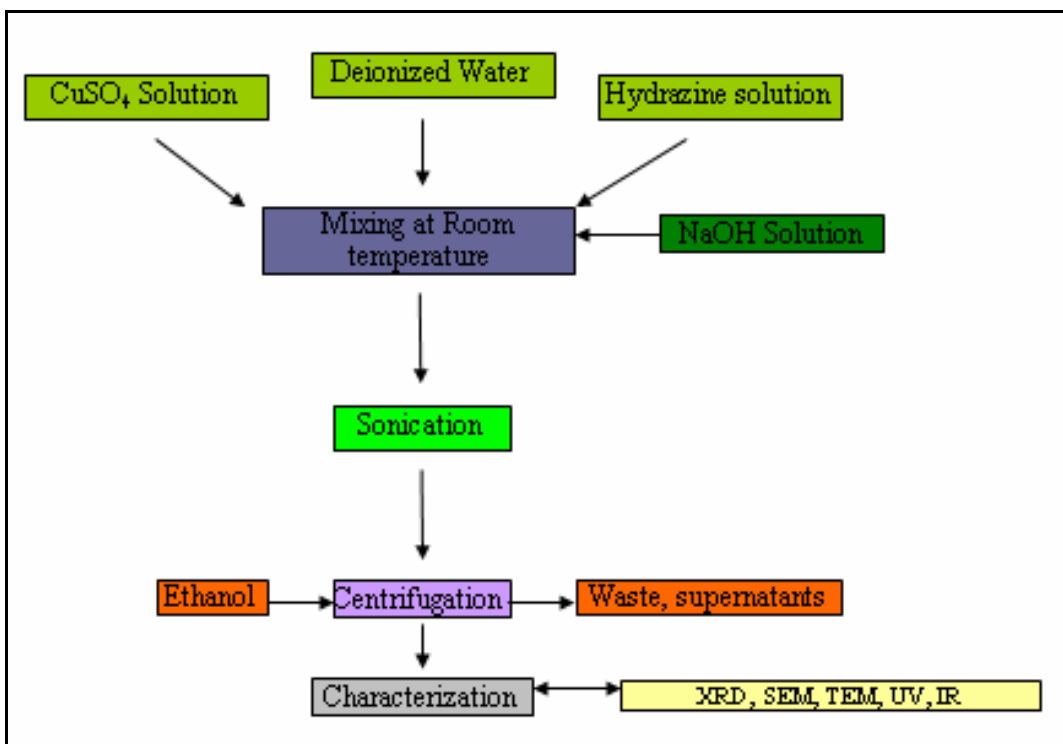


Figure 16. General procedure for copper nanoparticle synthesis in aqueous media using hydrazine as reductant agent.

3.2.2 Cu(II) reduction by ethylene glycol

A Cu(II) acetate solution in ethylene glycol was added into a three-neck flask containing a boiling ethylene glycol solution at a predetermined NaOH/Cu mole ratio, (R'). Copper concentration varied between 0.016 and 0.064M and 'R' ranged from 0.016 to 0.8M. The experimental set-up considered the use of a condenser to recover volatilized solvent (Figure 17). The experiments were carried out at 200 rpm of stirring intensity using a mechanical stirrer. Reacting solutions were heated at different heating rates and powers by a suitable control of the power of the mantle heater device. At the end of the reaction time, the polyol solution containing Cu particles was allowed to cool down. Copper nanoparticles were

recovered by centrifugation and washed in ethanol twice prior to their storage and characterization. A detailed diagram showing the most relevant aspects in polyol copper nanoparticles synthesis is presented in Figure 18.

Copper acetate, mantle heating power (MHP), PVP, and NaOH concentrations used in copper nanoparticles synthesis through the polyol process, are presented in table 4, and the most important conditions used to enhance the nanoparticle synthesis are presented in table 5. the reaction time is not presented but ranged between 30s to 1h.

Table 4: Concentration of reactants used in this work for copper nanoparticles synthesis in EG media.

	J	K	L	M	
[M] Cu(CH ₃ CO ₂) ₂	0.016	0.064			N
%MHP	50	100			O
[M] PVP	1.00E-07	5.00E-07			G
[M] NaOH	0.016	0.16	0.64	0.8	H

Table 5: More representative EG synthesis condition used in this work, (Based in table 5)

Parameter unchanged	Parameter changed	
JO	JN	KN
JN	KO	
JN KO	JG	KG
JN KO	JH	KH
JN KO	LH	MH

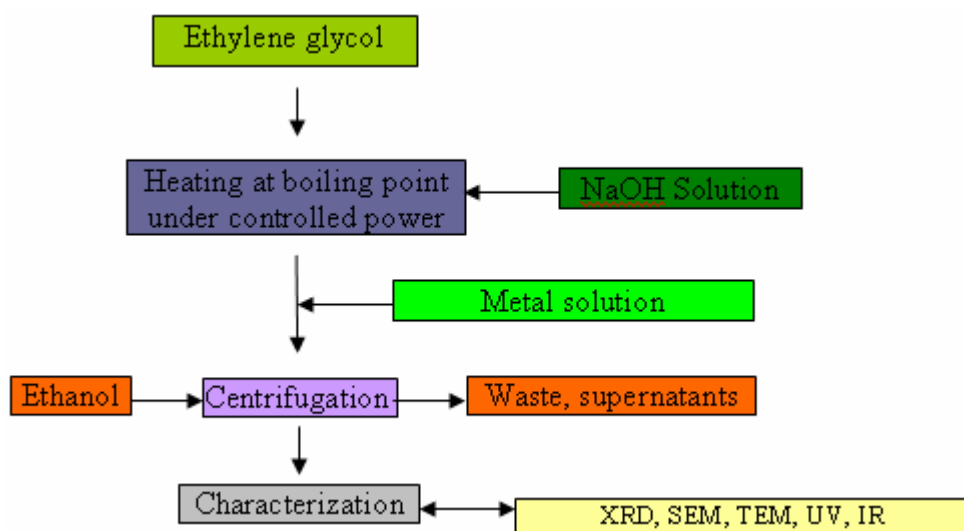
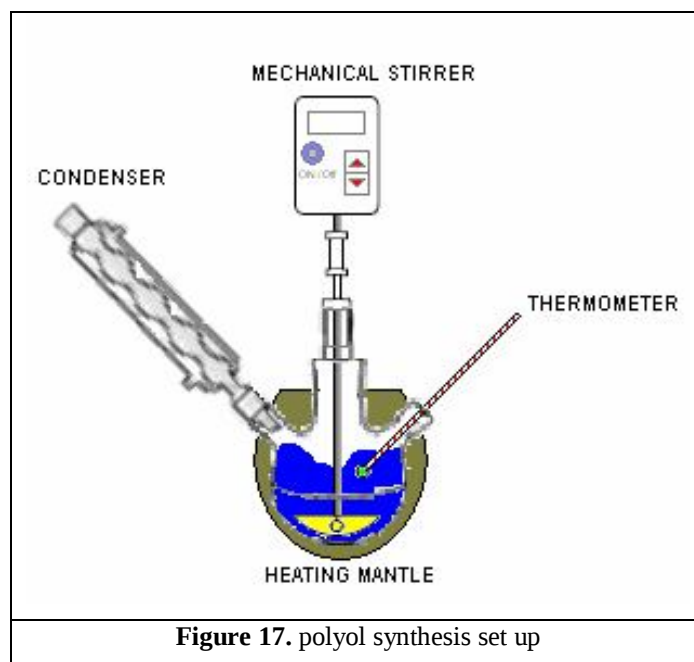


Figure 18. General procedure for copper nanoparticle synthesis in polyol.

3.3 Nanofluid Preparation

Cu nanoparticles produced by the above described methods were dispersed in ethylene glycol with normal and intensive sonication. ‘Normal sonication’ consider a sonication time of 15 minutes only (non treated samples is the denomination give to that samples in following discussions). In turn, under ‘sonication under intensive conditions’ the suspension was treated by prolonged ultrasonication cycles (up to 7 hours - treated samples is the denomination given to theses samples in following discussions). A detailed diagram showing the more relevant aspect in copper nanofluid preparation is shown in figure 19.

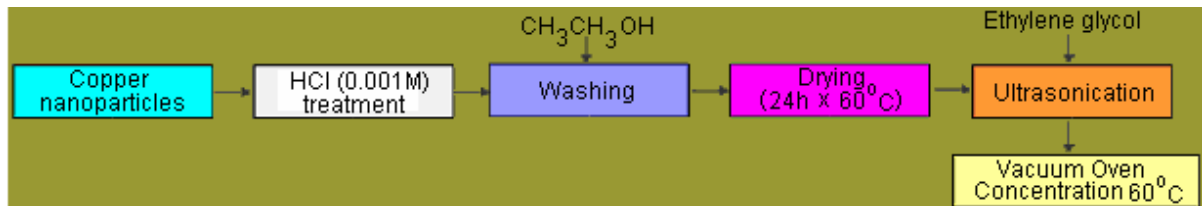


Figure 19. General nanofluid preparation procedure

3.4 The Hot-Wire Device set-up: design description and calibration

The hot-wire device to measure thermal conductivity of produced nanofluids, (figure 14 and 20), consisted of a platinum wire coated with a polyester enamel that is immersed in the test fluid. This Pt wire is used as both temperature sensor and heat source. In order to improve accuracy in the measurements of the thermal conductivity coefficients the wire resistance was measured using an unbalanced Wheatstone bridge to reduce the impedance error. A Wheatstone bridge contains three known and one unknown resistance, (the platinum wire). This system also required a voltage source and voltmeters, (data acquisition board). The cell consists of a two-walled glass cylinder, where the space between walls is empty. The

nanofluid is fed into inner cylinder to decrease the influence of the external environment. Then, the cell containing the nanofluid is placed into a high-accuracy cooling system and stabilized for one hour before reading the data. Details of the resistances and the experimental setup are presented in table 6.

Table 6: TWH apparatus, Part description

Item	Qty	Description
DC Power Supply	1	VIO ATX 12V power supply ky 550ATX
Data Acquisition Board	1	National Instrument NI-4350
Platinum Wire	1	AM-Systems Isonel Coated platinum wire, 25 μm bare, 28 μm coated 100 mm length
Resistance: R1 and R2	2	Precision resistor co, 250 Ω 0,005% accuracy
Resistance: R3	1	Precision resistor co 25 Ω 0,05% accuracy
Cylinder cell	1	12.6 mm inner wall, 20.0mm outer wall, 210 cm length.
Cooling system		Thermo electron corporation, digital one nestlab Rte 7, (temperature precision: 0.01 Celsius degrees).

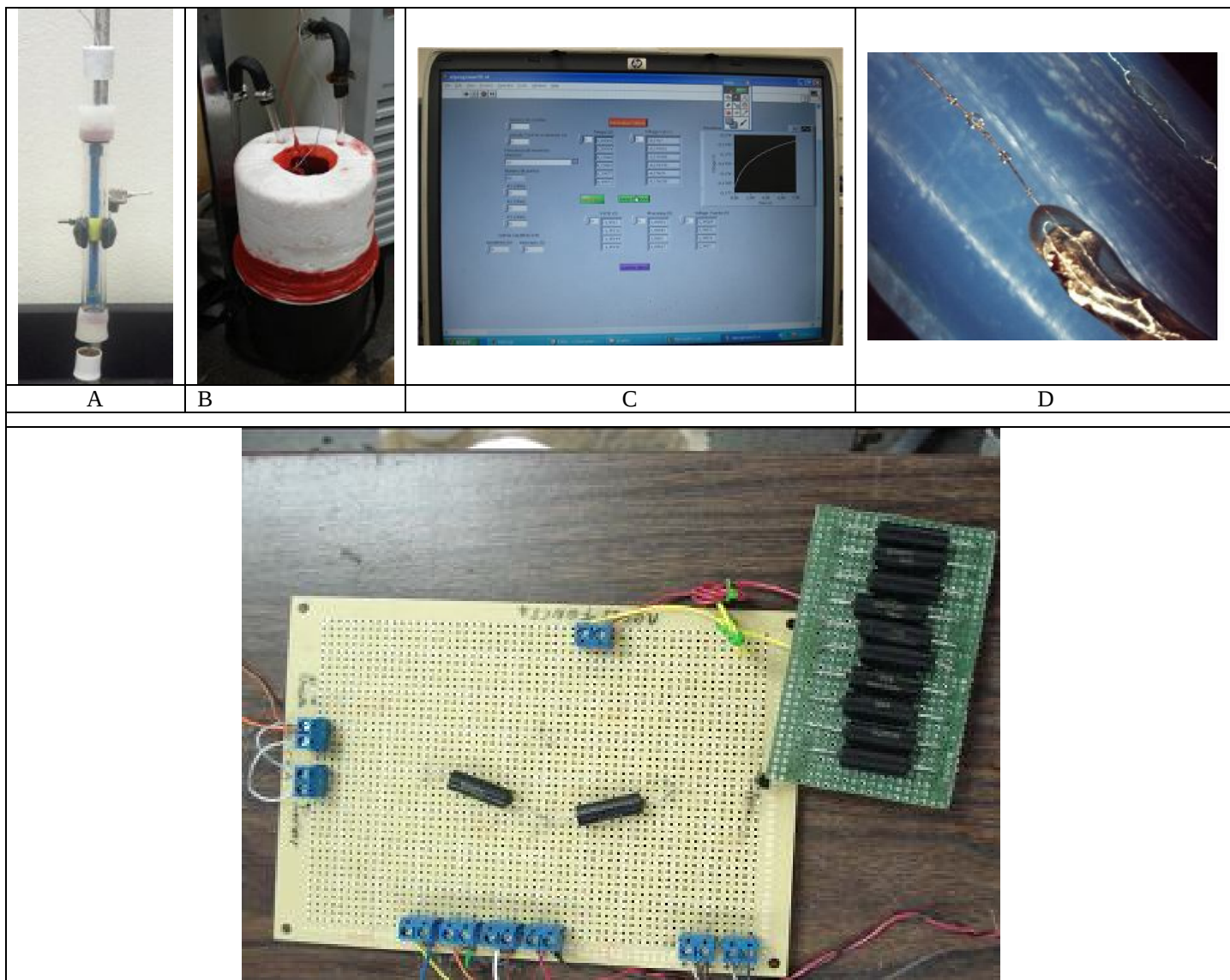


Figure 20. Photos of thermal conductivity measurement equipment build for this work, A: Measuring cell, B: Cell Enclosure, C: Controlling software, D: 28μm Wire – connector Connection, E: Wheatstone Bridge.

In a balanced Wheatstone bridge it is possible to relate the unknown resistance value with known resistances, a first step system calibration is required so that the equation 29 can be satisfied as well as possible, (figure 21).

$$\frac{R_1}{R_2} = \frac{R_w}{R_3} \quad (30)$$

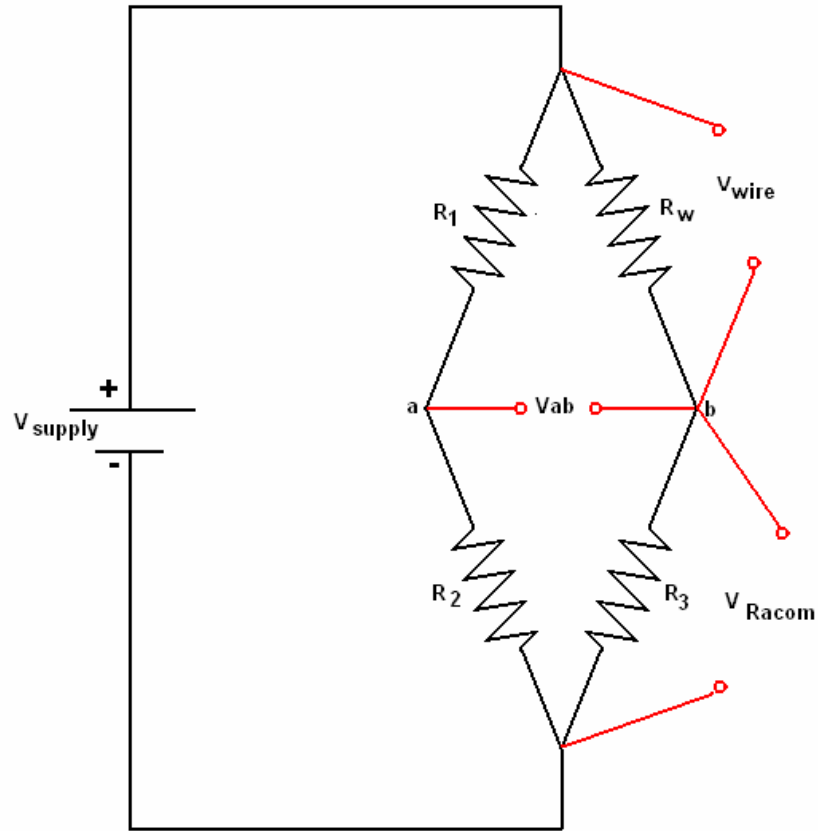


Figure 21. Wheatstone bridge with description of parts and voltages.

After determining R_3 , the system is energized and the wire resistance determined by using equation 30a.

$$R_w = R_3 \frac{V_{\text{supply}} R_1 + V_{ab} [R_2 + R_1]}{R_2 V_{\text{supply}} - V_{ab} [R_2 + R_1]} \quad (30a)$$

A data acquisition board is used to monitor the voltage of power supply, V_{ab} , wire voltage, (used to determine the current through the wire and power dissipated by it) and voltage passing through R_3 during eight seconds, at 0.1 seconds intervals. The data acquisition board is programmed to turn on and turn off the bridge as well as starting and finishing each voltage measurement cycle. Since all elements in the circuit, (excluding the wire) must reach a stable condition; only the data generated after 2 seconds will be considered for subsequent calculations of thermal conductivity.

In order to correlate the wire resistance with the fluid (ethylene glycol) temperature surrounding the wire, a calibration curve must be first obtained. The wire resistance will be measured for a set of prescribed temperatures. In an effort to increase the accuracy in the measurements, the resistance at a given temperature will be reported as the average of five measurements; the experimental error, (M_{axerr}), was calculated from the difference between high and low values, (table 7 and figure 22).

Table 7: Data recorded for obtain the calibration equation that correlated the resistance wire with temperature.

T(°C)	Resistance (Ω)	Maxerr R(T)
0,00	18,63892	0,0008
20,00	19,97688	0,00007
24,50	20,28702	0,00005
25,00	20,31904	0,00009
25,50	20,35042	0,00005
30,00	20,68812	0,00009
60,00	22,7685	0,0004

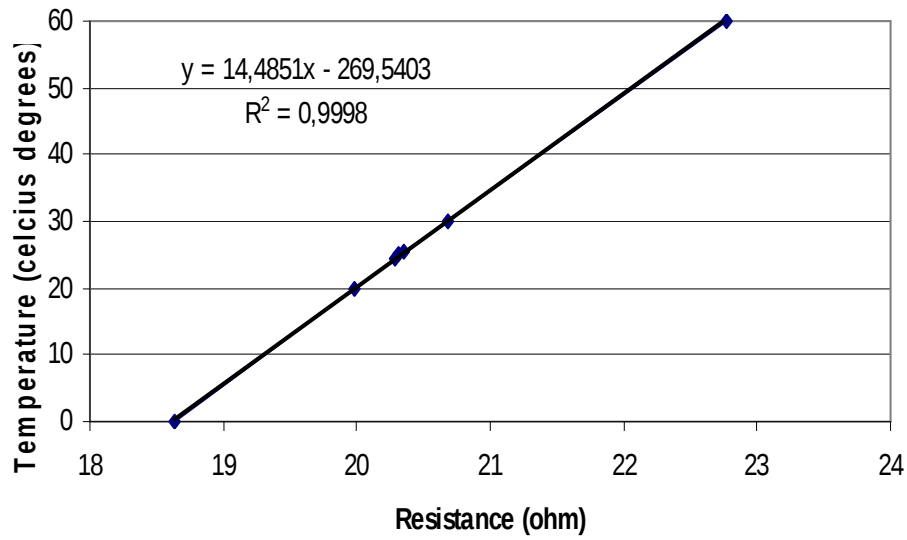


Figure 22. Relationship between wire temperature and wire resistance.

As figure 22 shows, the relation between the wire resistance and wire temperature is linear ($R^2=0.9998$) between 0.00°C and 60.00°C. The selection of a long range in temperature allowed decreasing the experimental error.

For thermal conductivity measurements, wire resistance is recorded for prescribed times. Next, the temperature is determined from the above described temperature – resistance calibration curve. Then, after linearizing the temperature- $\ln(\text{time})$ curve, the slope is calculated and used in equation 29 to calculate the thermal conductivity. The ‘q’ term, that represents the power dissipated by wire, is determined from the measurements of the wire and R1 associated voltages using equation 31. The ‘q’ term is calculated as the average of q_i ; the experimental error is calculated from the difference between the highest and lowest measured values.

$$q_i = \frac{V_{wire} * V_{Racom}}{R_3} \quad (31)$$

The determination of the “C” parameter, (see equation 29), demands to know beforehand the thermal conductivity for reference fluids and determine the ratio between ‘K’ measured in the transient hot wire equipment and ‘K’ reported in literature. We used water and ethylene glycol for such calculations (table 9).

Table 8. Ethylene glycol and water thermal conductive measurements (used for equipment calibration).

Substance	Reported k (interpolated) W/(mK)	Measured k W/(mK)	k measured /k reported
Water	0.605	0.678	1.121
Ethylene glycol	0.249	0.309	1.239

It is also possible to estimate the accuracy of our measuring system by registering repeatedly ‘K’ values followed by a statistical analysis. Table 9 shows that the difference in thermal conductivity between samples is in the same order that standard deviation for each sample. It was on agreement with expected values where the average value per sample was typically between 3 times the standard deviation. Accordingly, the variation in the measured coefficient values ($\Delta / \bar{A} * 100$), can be considered low enough for our evaluations.

Table 9. Thermal conductivity measurement accuracy for ethylene glycol.

Test number	average thermal conductivity Without considering C constant W/(mK)	Standard deviation (σ) W/(mK)	Difference between measures (Δ) W/(mK)	$\Delta/\bar{A} \cdot 100$
1	0,312	0.00204	0,00323 (1-2)	1,04
2	0,309	0.00302	-0,00598 (2-3)	-1,92
3	0,315	0,00280	-0,00275 (1-3)	-0,88
Average value between samples ($\bar{A}$)	0,312	number samples per test	20	

Figure 23 shows the temperature- $\ln(\text{time})$ plots for water and ethylene glycol. The observed variation between the set of measurements is attributed to random phenomena including temperature variations.

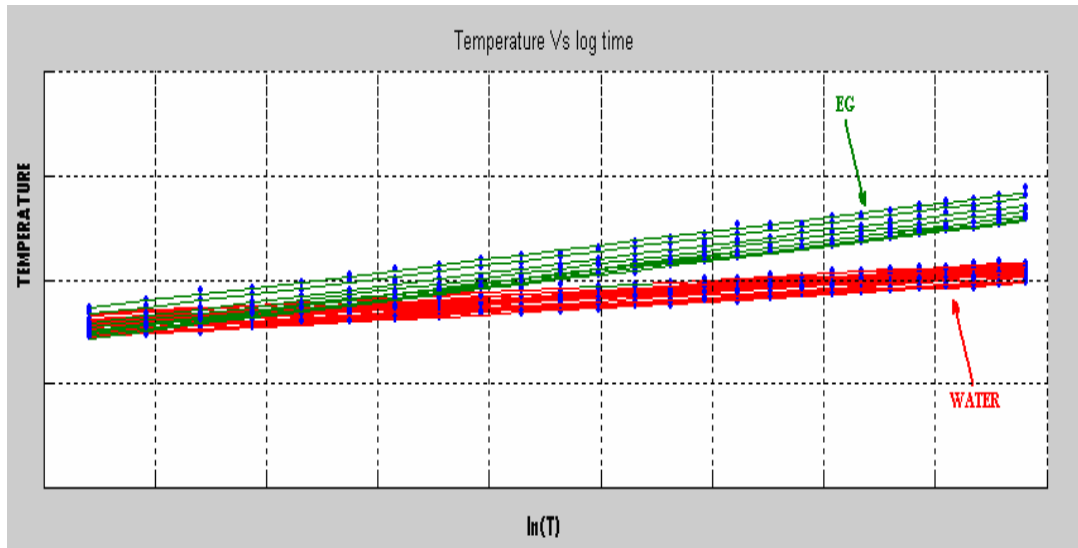


Figure 23: Temperature vs. Ln (Time(Sec)) Water and ethylene glycol.

Due to a possible degradation in coating it is necessary to make measurement for base fluid each time a nanofluid is evaluated.

3.5 Characterization Techniques

Structural analysis of the powders was carried out by x-ray diffraction (XRD) using the Cu-K α radiation. The average crystallite size of produced powders was estimated by using the Scherrer's equation for the (111) and (200) peaks. UV-vis spectroscopy was used to determine optical properties of the Cu nanoparticles in different suspending media. Particle morphology was examined by high-resolution transmission electron microscopy (HRTEM) and scanning electron microscopy (SEM).

4 RESULTS AND DISCUSSION

4.1 Synthesis of Copper Nanoparticles

Copper nanoparticles were synthesized by reduction of cupric species in aqueous (hydrazine) and non-aqueous (ethylene glycol) media.

4.1.1 Cu(II) reduction in hydrazine

The effect of reaction time, copper sulfate concentration, hydrazine concentration, amount of NaOH and type of surfactant (SDS or CTAB) on the formation of nanocrystalline copper and average crystallite size was evaluated.

4.1.1.1 Structural characterization by x-ray diffraction (XRD)

4.1.1.1.1 Effect of reaction time

Time is a very important parameter in nanoparticle synthesis. As an empirical rule, a decrease in time for nanoparticle nucleation produces a decrease in the nanoparticle size, due to more small metal nucleus appear per time unit. Figure 24 shows typical XRD patterns for the solids synthesized at different reaction times from 0.0016M Cu(II) in 0.059M aqueous hydrazine solutions. The solids formed at earlier times consisted of partially reduced cuprous oxide (Cu_2O). The drop in the intensity of the Cu_2O peaks and the simultaneous increase and sharpening of the peaks corresponding to elemental copper, suggested that the final formation of elemental Cu from starting Cu(II) solutions took place through the formation of partially reduced Cu(I) oxide as an intermediate phase. This intermediate should have been

redissolved at prolonged reaction times and finally reduced to the zero valence state. The average crystallite size for Cu nanoparticles using 0.0016M Cu and 0.059M N_2H_4 , varied from 25.0 nm to 27.4 nm when the reaction time was prolonged from 12 hours to 24 hours, respectively. The lattice parameter for the solids produced after 12 hours of reaction was 3.618 Å, which is in good agreement with the bulk value of 3.615 Å (PDF # 00-004-0836 XRD data from MATCH software, see section 2.51).

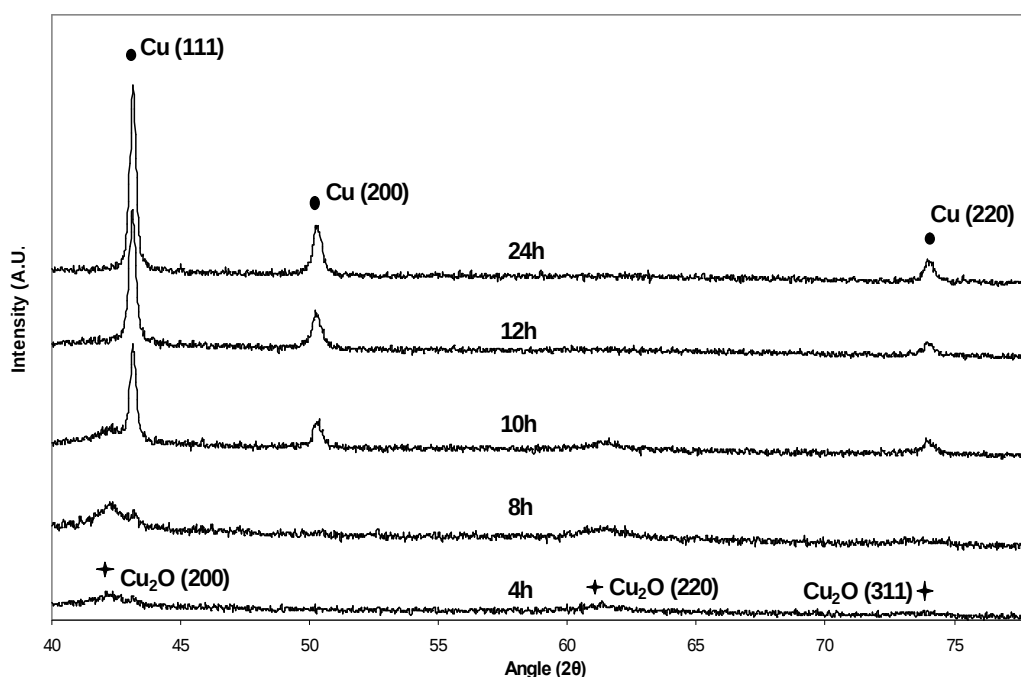


Figure 24. XRD patterns of powders synthesized at different reaction times. Reactants concentrations were 0.0016M Cu and 0.059M N_2H_4

Figure 25 and 26 show the XRD pattern for solid produced after reduction of 0.064M Cu(II) in 0.059M aqueous hydrazine solutions and 0.016M Cu(II) in 0.24M aqueous hydrazine solutions, respectively. The sequential formation of cuprous oxide (Cu_2O) followed by its consumption and posterior formation of elemental Cu was observed again. Crystallite size for copper nanoparticles obtained under 0.064M CuSO_4 , 0.059M N_2H_4 , and 34 hours of reaction

was 30,2nm (figure 25). The average crystallite sizes were 20.7nm, 22.3nm and 25.7nm when 0,016M CuSO_4 and 0,24M N_2H_4 were used and after 1, 2, 4 hours of reaction, respectively (figure 26). The comparison of the XRD data in figures 25 and 26 allows us to suggest that a rise in the initial concentration of Cu species will not only delay the Cu formation reaction but also will be conducive to larger crystallite sizes. Furthermore, the average crystallite size could be changed just by a suitable control of the reaction time under more dilute Cu(II) concentration conditions. On a mechanistic point of view, our data clearly evidenced the formation of partially reduced Cu(I) oxide as intermediate phase. The stability of this intermediate would be considered the rate limiting step in the complete Cu(II) reduction process due to first is necessary their dissolution before copper appears..

It is very important to take into account that copper nanoparticles can oxidize very quickly. Accordingly, all copper nanoparticles synthesized in this work were always maintained in ethanol media for storage.

The dramatic effect of the reactants concentrations (Cu ions and hydrazine) on the rate of the Cu forming reaction will be discussed in the following sections.

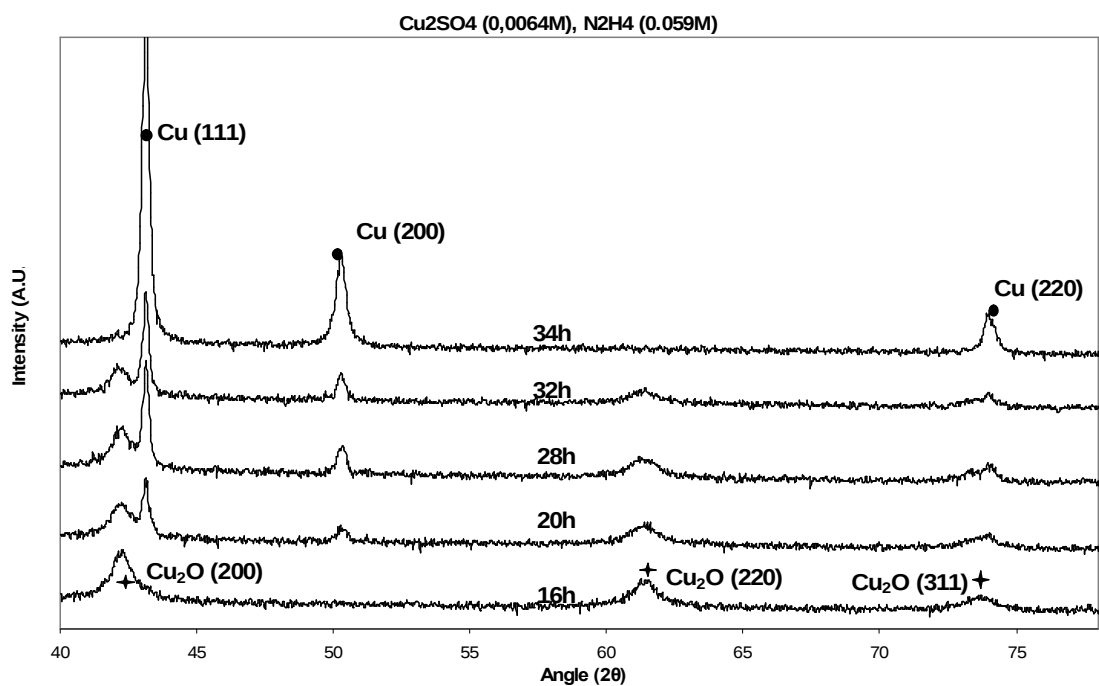


Figure 25. XRD patterns of powders synthesized at different reaction times. Reactants concentrations were 0.0064M Cu and 0.059M N₂H₄

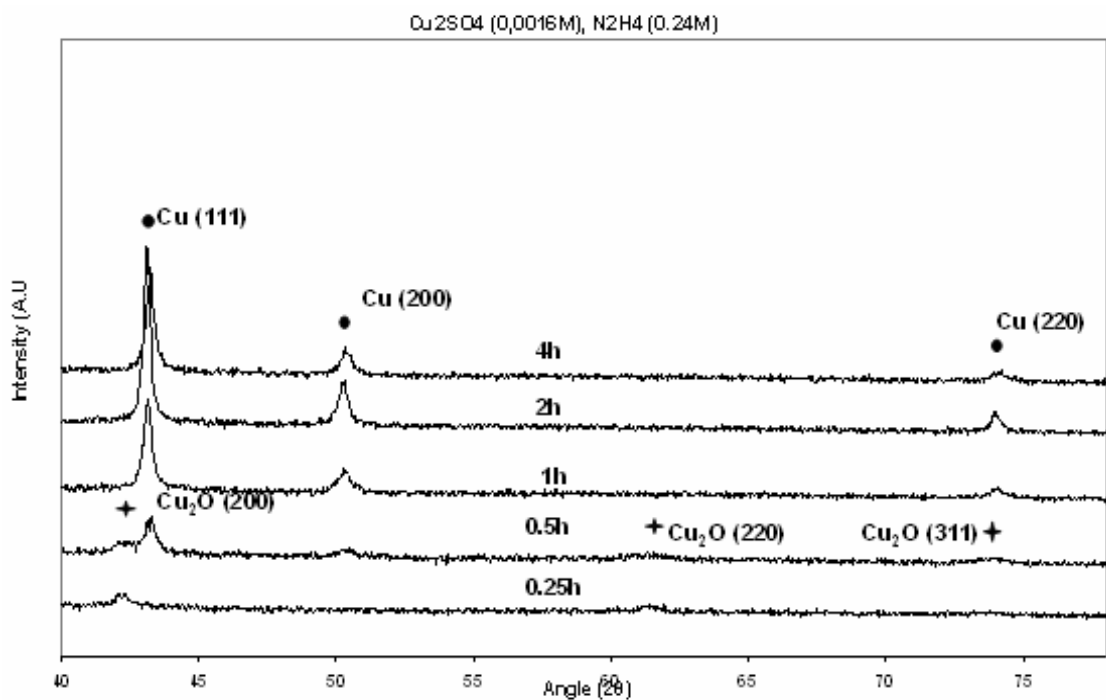


Figure 26. XRD patterns of powders synthesized at different reaction times. Reactants concentrations were 0.0016M Cu and 0.24M N₂H₄

4.1.1.1.2 Effect of the concentration of Cu(II) ions

In order to evaluate the effect of the initial concentration of Cu(II) species on the rate of formation and the corresponding average crystallite size of Cu nanoparticles produced, a 0.059M hydrazine solution was contacted with Cu(II) solutions in the range of concentrations between 0.0016M and 0.0064M. The reaction was interrupted when the complete reduction of Cu was realized. Figure 27 shows the XRD patterns for the solids produced at different initial Cu(II) concentration. The reaction times required for complete reduction of Cu(II) species were 12h (A), 24h (B), 28h (C), and 34h (D). Only peaks corresponding to elemental Cu were detected, suggesting the complete reduction of Cu(II) species. It was observed that the lowering of the Cu(II) concentration made the time required to form elemental Cu shorter. As expected, the reaction time was shortened from 34 hours to 12 hours when the Cu(II) concentration dropped from 0.0064M down to 0.0016M. The corresponding average crystallite sizes ranged between 25nm and 30nm.

The enhancement observed in the Cu formation can be a consequence of the ratio Cu(II)/reductant, which is increased when more dilute Cu ion concentrations are used. In other words, the lower the starting Cu ions concentrations, the higher the availability of reducing species and, consequently, a higher reduction potential in the solution should be expected.

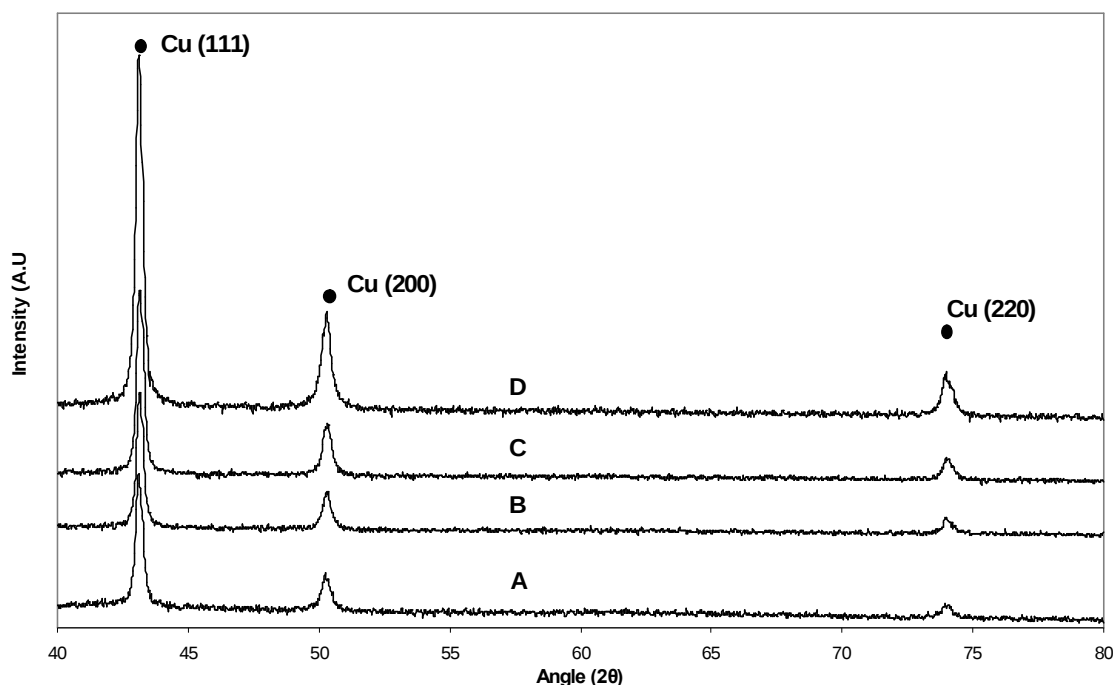


Figure 27. XRD patterns of powders synthesized at 0.059M N_2H_4 and different Cu concentrations. A: 0.016M Cu; B: 0.032M Cu; C: 0.048M Cu and D: 0.064M Cu.

Considering the decrease in copper reduction time and the correspondent decrease in crystallite size, the concentration of copper of 0.016M will be used for the subsequent analysis.

4.1.1.1.3 Hydrazine concentration effect

The effect of hydrazine concentration on the kinetic of Cu(II) reduction and the corresponding crystal size was also evaluated. Figure 28 shows the XRD patterns of the solids produced from a 0.0016M Cu(II) solution and different concentrations of hydrazine. Here again, the reduction reaction was interrupted once the formation of elemental Cu was completed. As evident, the reduction of Cu(II) species required shorter times when the concentration of hydrazine was increased from 0.059M up to 0.70M. The larger

concentrations of hydrazine should have promoted the establishment of stronger reduction conditions and a larger availability of reducing species that accelerated the Cu(II) reduction reaction. The corresponding reaction times and average crystallite size varied from 12 hours to 30 minutes and from 25.0 nm to 17.8 nm, respectively.

The data in table 10 evidences that an increase in hydrazine concentration lead to a decrease in crystallite size. Also, this behavior can be explained by the greater availability of reducing agent that would have accelerated the reduction rate and, hence, promoted the nucleation rate at the expense of particle growth.

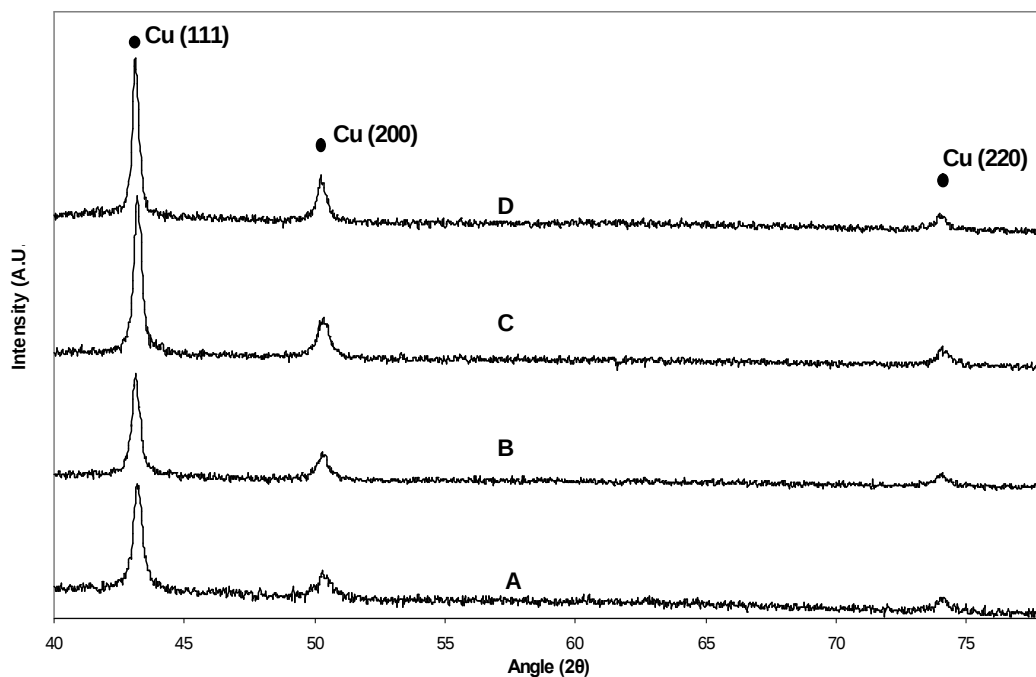


Figure 28. XRD patterns of Cu powders synthesized at different concentrations of hydrazine. A: 0.7M N_2H_4 ; B: 0.24M N_2H_4 ; C: 0.12M N_2H_4 and D: 0.06M N_2H_4 . The Cu concentration was 0.0016M.

Table 10. Crystallite size as function of hydrazine concentration. Cu concentration was 0.016M.

Hydrazine concentration (M)	Average crystallite size (nm)
0.70M	17,8
0.24M	20,7
0.12M	21,0
0.06M	25.0

Considering the result above presented, a hydrazine concentration of 0.70M was selected for the subsequent analysis.

4.1.1.1.4 Effect of the NaOH concentration

Equation 2 in page 17 suggested that the increase of pH in aqueous media would favor the progress of the copper reduction reaction. The probable kinetic enhancement could also be conducive to a reduction in crystallite size because of the enhancement of nucleation rate. Although the use of higher concentrations of hydrazine were conducive to the rise in the solution pH, we wanted to investigate if the observed enhancement on the rate of the copper forming reaction is only because of the optimum concentration of hydrazine, the solution pH or both. For this purpose, all experiments were carried out with a 0.016M Cu and 0.24 M of hydrazine solutions. The reaction time was kept constant at 1 hour, (this time was long enough to assure the complete reduction of a 0.016M Cu solution by using 0.24 M of hydrazine solution). The amount of sodium hydroxide was controlled by selecting a NaOH/Cu mole ratio (R_N), between 1 and 50.

Two experimental procedures were followed. In the first one, the NaOH was added to the Cu solution in water, mixed for 18 hours at room-temperature and followed by the addition of

the hydrazine. The reaction was stopped after one hour of contact. As said, this reaction time was long enough to produce elemental Cu in the absence of NaOH, (figure 28). The obtained results are shown in figures 29 and 30. Figure 29 shows the XRD patterns for the solids produced after mixing Cu solution with NaOH. The poor crystallinity of the solids (probably copper hydroxide) is evidenced by the absence of any clear diffraction peak. In turn, figure 30 shows the XRD patterns for the solids recovered after the previously formed amorphous solid was contacted with hydrazine. Only poorly crystalline Cu(I) oxide was observed irrespective of the R_N value. Evidently, the formation of metallic Cu was completely inhibited by the formation of the solid amorphous intermediate (cupric hydroxide). This intermediate should have been well stabilized under the experimental conditions making their further reduction a extremely slow process.

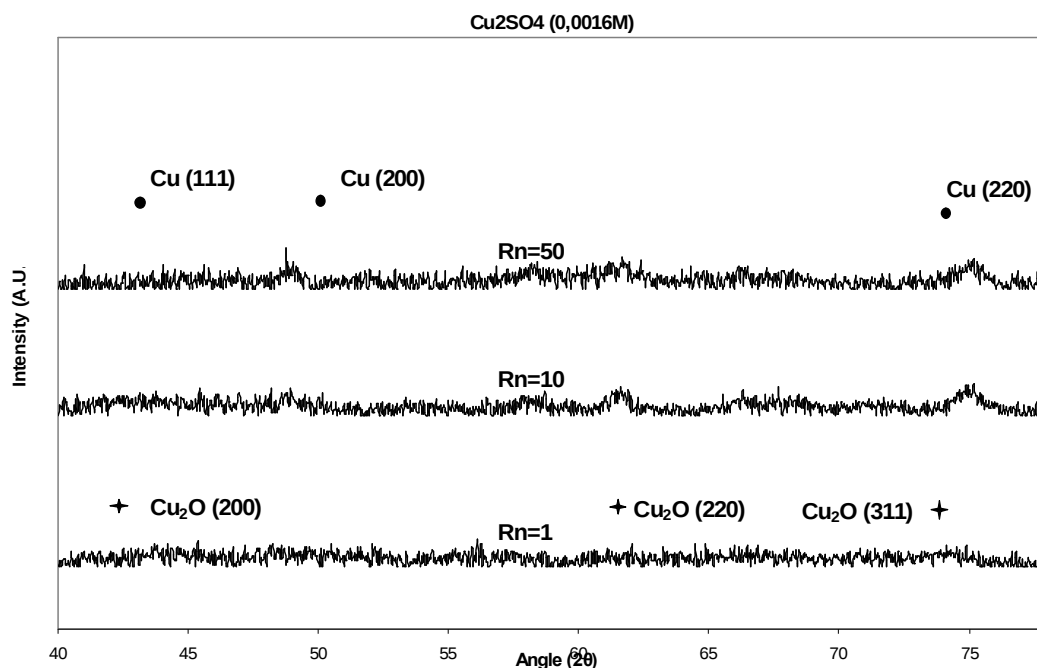


Figure 29. XRD patterns for recovered solids after 18h, when NaOH is add to a copper sulfate solutions (with out hydrazine additions)

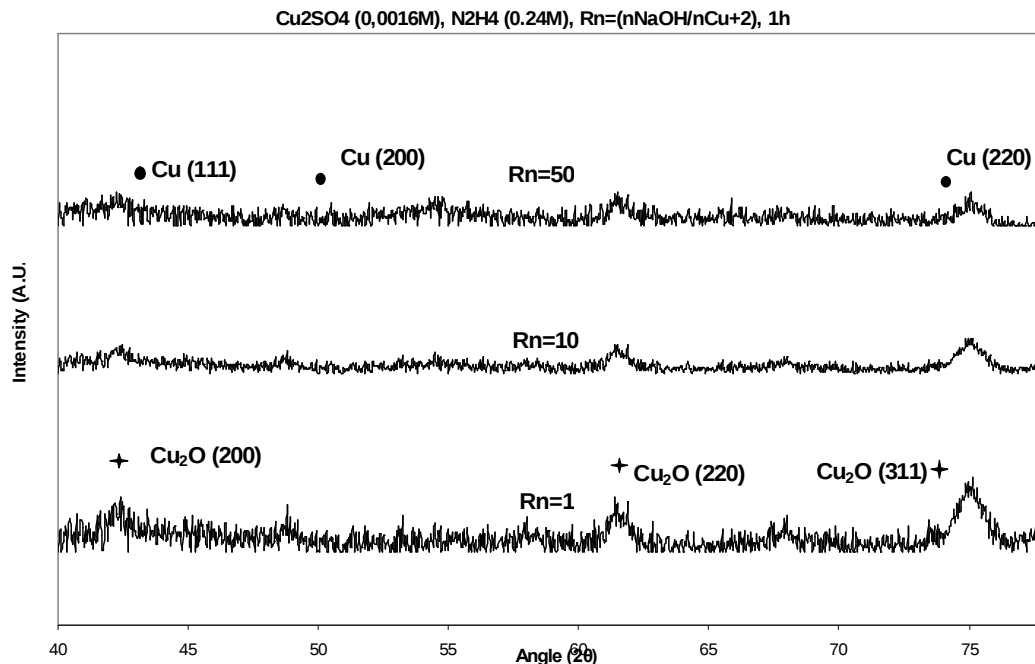


Figure 30. XRD patterns of recovered solids after 1h of reaction with hydrazine and 18h aged copper sulfate solutions with sodium hydroxide.

In the second approach, the NaOH was directly contacted with an aqueous solution containing Cu ions and hydrazine at room temperature. Once again, the reaction was stopped after one hour. Figure 31 shows the XRD patterns for the solids produced at different R_N values. Although the solids were more crystalline, only the peaks for Cu₂O were identified, suggesting that complete reduction of Cu(II) species did not take place.

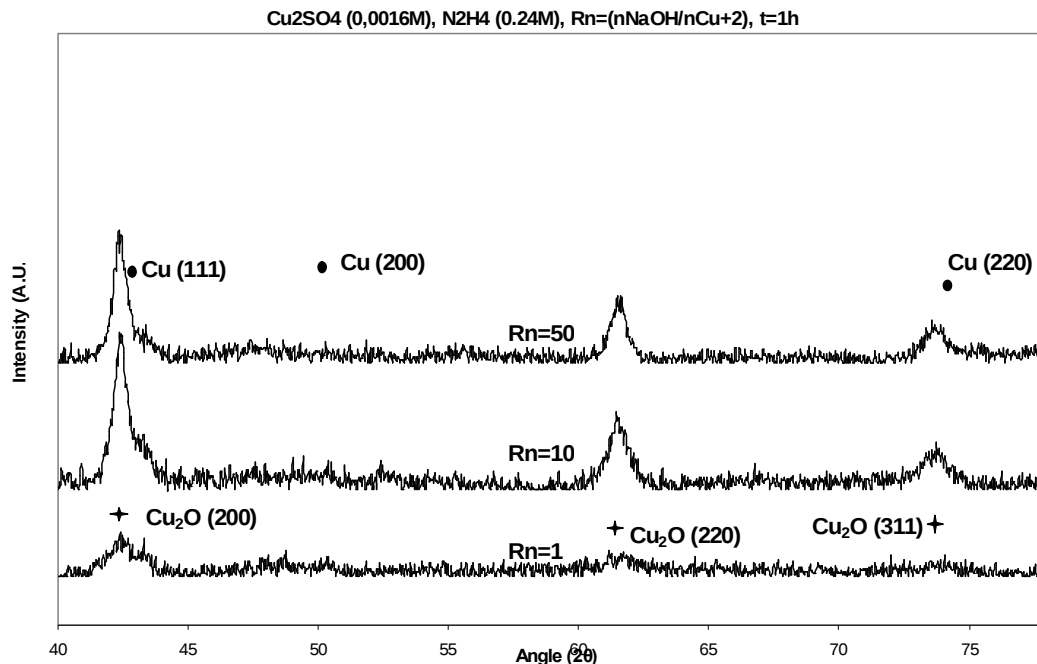


Figure 31. XRD patterns of recovered solids after 1h of reaction with pre mixed hydrazine – sodium hydroxide solutions and copper sulfate solutions.

Based on the above results, it is clear the null contribution of an excess of NaOH on the enhancement of the Cu reduction reaction. On the contrary, this excess of hydroxyl ions promoted the formation of an insoluble and stable intermediate (Cu hydroxide) that delayed the reduction reactions. In the best case scenario, only Cu(I) oxide was formed. Therefore, the previously showed results can be attributed exclusively to the effect of the hydrazine and not to the observed rise in pH.

The values of the variation in the Gibbs' free energy presented in pages 18 and 19, suggested that the reduction of copper by mean of hydrazine is a thermodynamically favored process. This trend should be even stronger in presence of an excess of NaOH. According to our

results, it was not the case because of the kinetic restriction involved with the high stability of the amorphous and Cu_2O intermediates formed at high NaOH amounts.

4.1.1.1.5 Effect of surfactants addition

Surfactants were used during the copper-forming reaction to prevent particle aggregation and inhibit crystal growth by mean of the interaction between polar groups and nanoparticle surface. For this purpose, two types of water-soluble surfactants were evaluated: sodium dodecylsulfate (SDS) and Cetyltrimethyl-ammonium bromide (CTAB).

4.1.1.1.5.1 Effect of SDS concentration

Copper reduction in hydrazine tests were carried out at different concentrations of SDS ranging from 0.00052M up to 0.01040M. The starting concentration of Cu(II) ions was 0,016M M in all experiments. The progress of the Cu(II) reduction process was monitored at different reaction times. Our results evidenced the strong dependence of the Cu formation with the SDS concentration. Figures 32 and 33 show the XRD patterns corresponding to the solids produced at different reaction times, when the SDS concentration was 0.00052 M and 0.0052 M, respectively. As evident, the higher the SDS concentration, the faster the copper formation; Cu and Cu_2O co-existed when the reaction took place in presence of 0.00052M of SDS and 0.5 hours whereas only elemental Cu was formed at a higher SDS concentration. SDS is acting not only as a surfactant agent but also as a catalyst for the copper reduction reaction. This catalytic effect can be a consequence of formation of copper dodecylsulfate that would be able to promote the copper reduction by acting as nucleation center, considering that copper dodecylsulfate can form micelle aggregates when its concentration is

higher than the critical micelle concentration [69]. The reducing capability of SDS species in aqueous phase should also be involved with the observed trends.

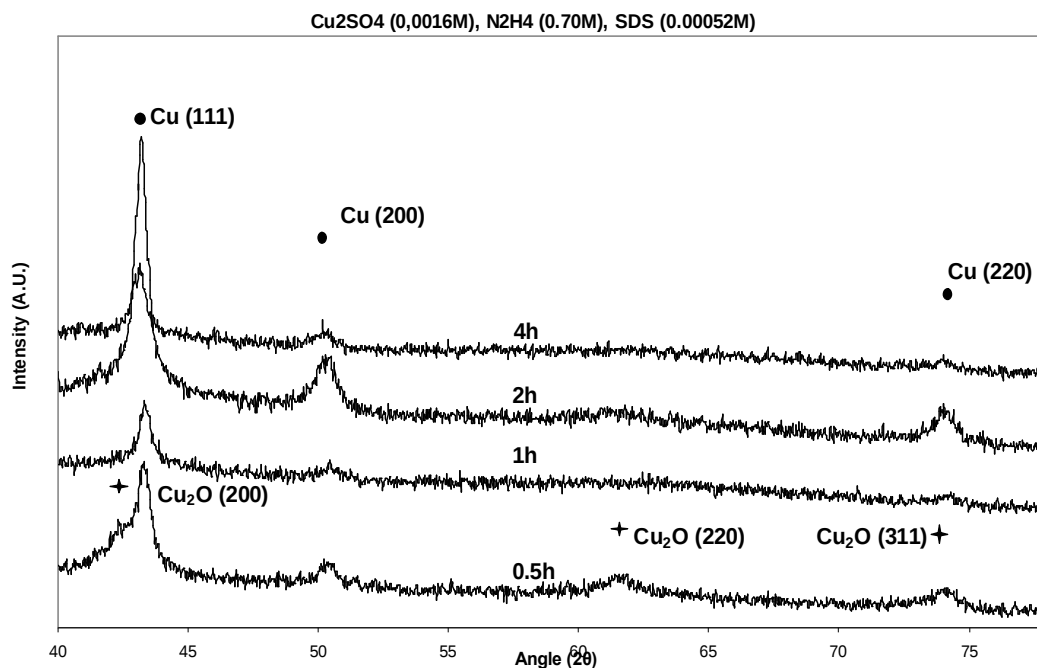


Figure 32. XRD patterns of recovered solids at different reactions time, Cu concentration was 0.0016M, Hydrazine concentration was 0.70M and SDS concentration was 0.00052M.

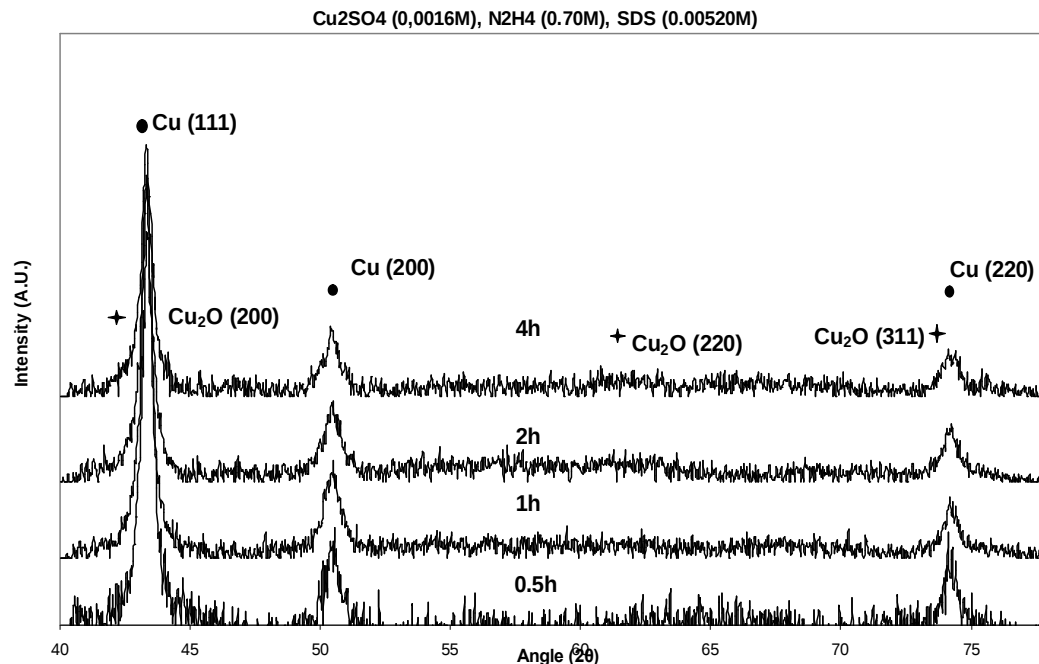


Figure 33. XRD patterns of recovered solids at different reactions time, Cu concentration was 0.0016M, Hydrazine concentration was 0.70M and SDS concentration was 0.00520M.

Table 11, summarizes the corresponding variation in the average crystallite size with respect to time when SDS concentration was CM, it is possible see the expected increase in crystallite size when is increased the reaction time maintaining constant the synthesis conditions.

Table 11. Variation in the average crystallite size with time. Cu concentration: 0.0016M, Hydrazine 0.70M and SDS 0.00520M.

Time (h)	Crystallite size (nm)
0.5	12,7
1	15,3
2	16,0
4	18,2

Table 12 shows the variation in crystallite size obtained at different concentration of SDS and a constant reaction time of two hours. The corresponding XRD patterns are shown in Figure 34. As seen, the increase in SDS concentration promoted the growth of the crystallites.

Table 12. Crystallite size as function of SDS concentration for 2 hours of reaction time, Cu concentration was 0.0016M and Hydrazine concentration was 0.70M.

SDS concentration (M)	Average crystallite size (nm)
0.00052	12,7
0.00260	14,5
0.00520	18,2
0.00780	20,7
0.01040	17,8

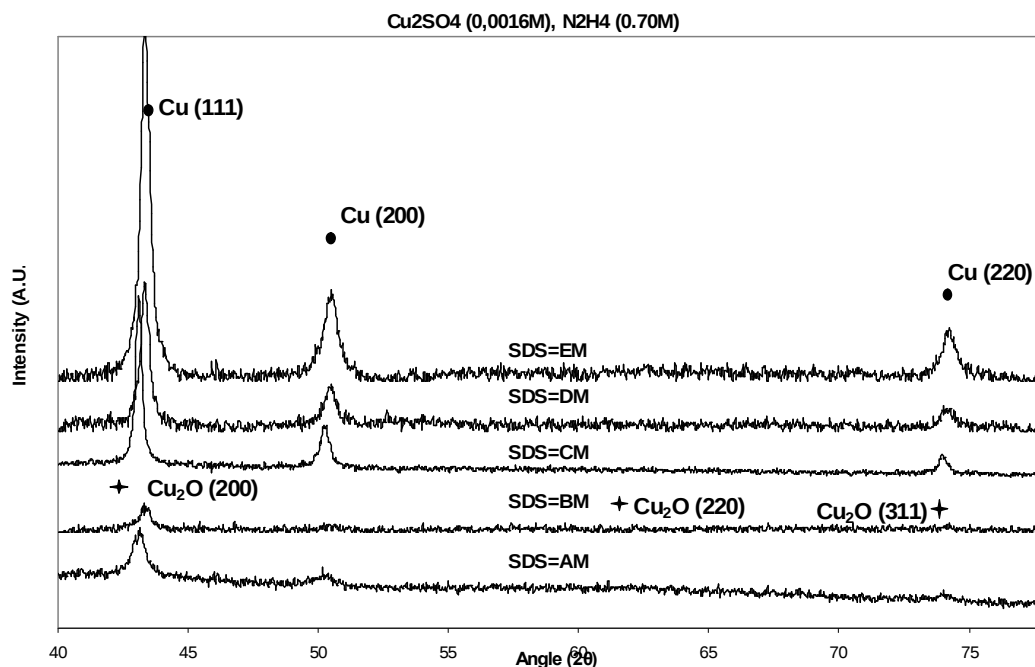


Figure 34. XRD patterns of recovered solids at different SDS concentration, Cu concentration and hydrazine concentrations were 0.0016m and 0.70m, respectively. The reaction time was 2 hours. AM=0.00052M, BM=0.00260M, CM=0.00520M, DM=0.00780M, EM=0.01040M.

On the above basis, SDS has proved to be an effective crystal growth inhibitor and also a catalyst of the reduction reaction. Nanocrystals produced in presence of SDS were pretty

stable in water even after prolonged times (above 24 hours). Although this behavior can be considered a consequence of the suitable coating of the nanocrystals with SDS, it also makes the particle removal a very difficult task. Since nanoparticles must be isolated from the aqueous phase to be re-suspended in target cooling liquid (ethylene glycol), the difficulty in their removal from water could be considered a serious impediment for the subsequent nanofluid preparation stage.

4.1.1.1.5.2 Effect of CTAB concentration

The time monitoring of the Cu formation was carried out at a CTAB concentration in the 0.00052M to 0.01040M range. Figures 35 and 36 show the XRD patterns corresponding to the solids produced at various reaction times and CTAB concentrations of 0.00052M and 0.0052M, respectively. XRD data confirmed the strong influence of CTAB on the formation of elemental copper. The most remarkable effect of CTAB was the decrease in the average crystallite size when very low CTAB concentration (0.00052M) was used. The average crystallite size varied from 17nm (in absence of CTAB) down to 15nm after a reaction time of 4 hours, is possible that CTAB form stable complexes and the time required for copper reduction increases and crystallite size decreases.

On the other hand, as Figure 36 evidences, an increase in the CTAB concentration will completely inhibit the formation of elemental copper; it was not detected even after 4 hours of reaction when a 0.0052M CTAB solution was used.

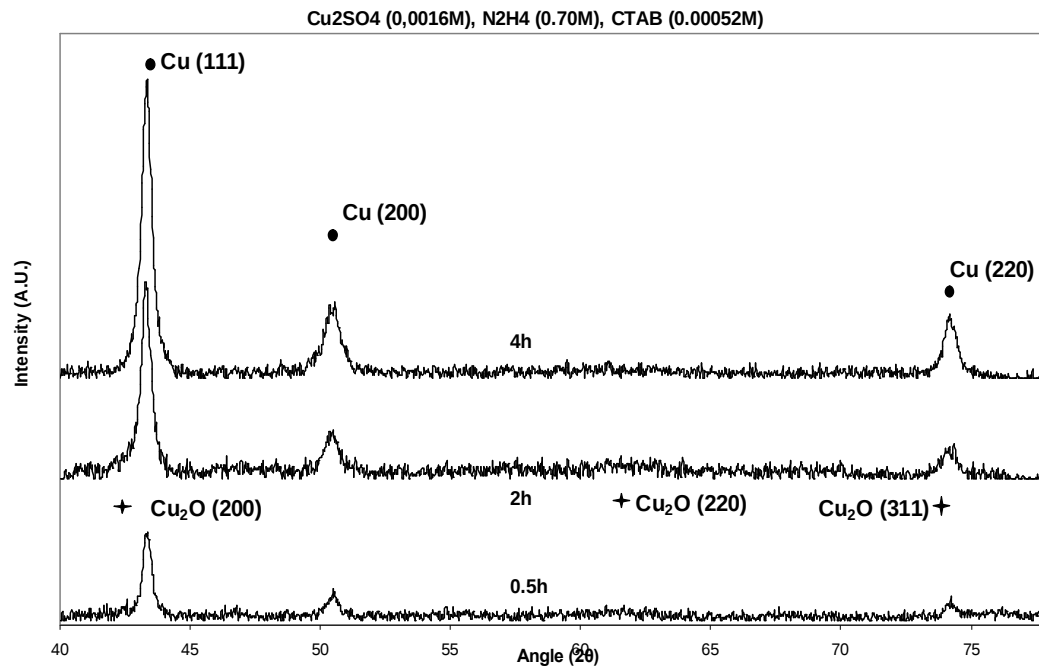


Figure 35. XRD patterns of recovered solids at different reactions time, Cu concentration was 0.0016M, Hydrazine concentration was 0.70M and CTAB concentration was 0.00052M.

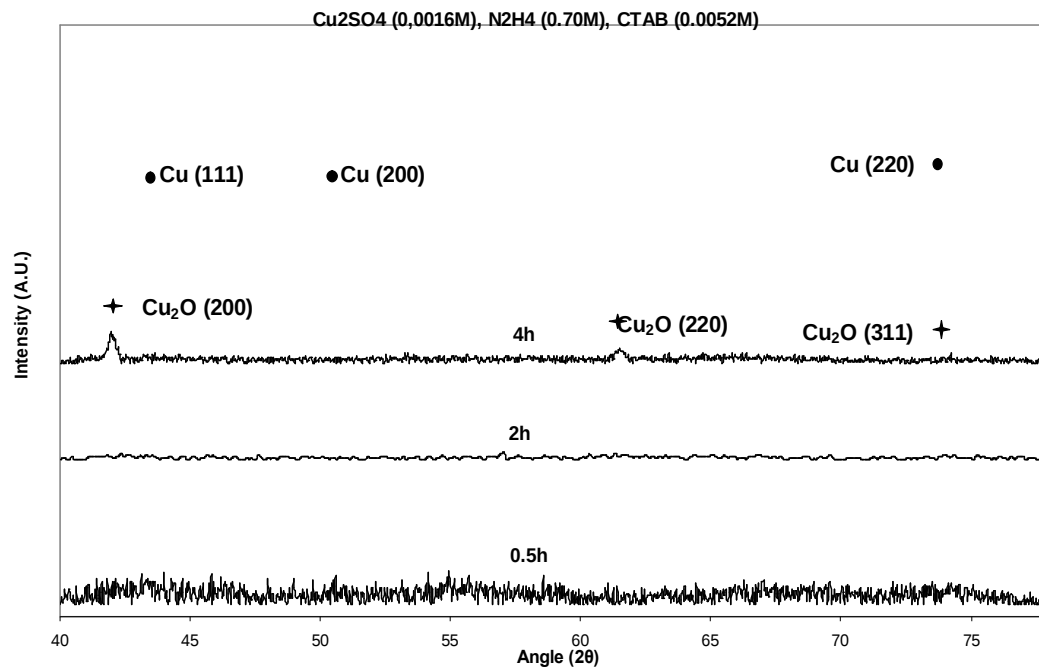


Figure 36. XRD patterns of recovered solids at different reactions time, Cu concentration was 0.0016M, Hydrazine concentration was 0.70M and CTAB concentration was 0.0052M.

As we discussed above, CTAB can be considered an effective growth-inhibitor agent but at expenses of the delay on the copper formation. In order to determine the effect of CTAB concentration on the average crystallite size of the products, we conducted additional experiments at various concentrations of CTAB whiled the reaction time was kept constant at 4 hours. Figure 37 shows the XRD patterns corresponding to these experiments. It is observed that Cu formation could be realized only at a low CTAB concentration.

Also in this system, the produced Cu nanoparticles became quite stable in water when synthesized in the presence of CTAB. Attempts to coagulate the nanoparticles by NaCl and Ethanol were not successful. This difficulty in removing the nanoparticles from water could be considered a serious obstacle for the subsequent nanofluid preparation stage.

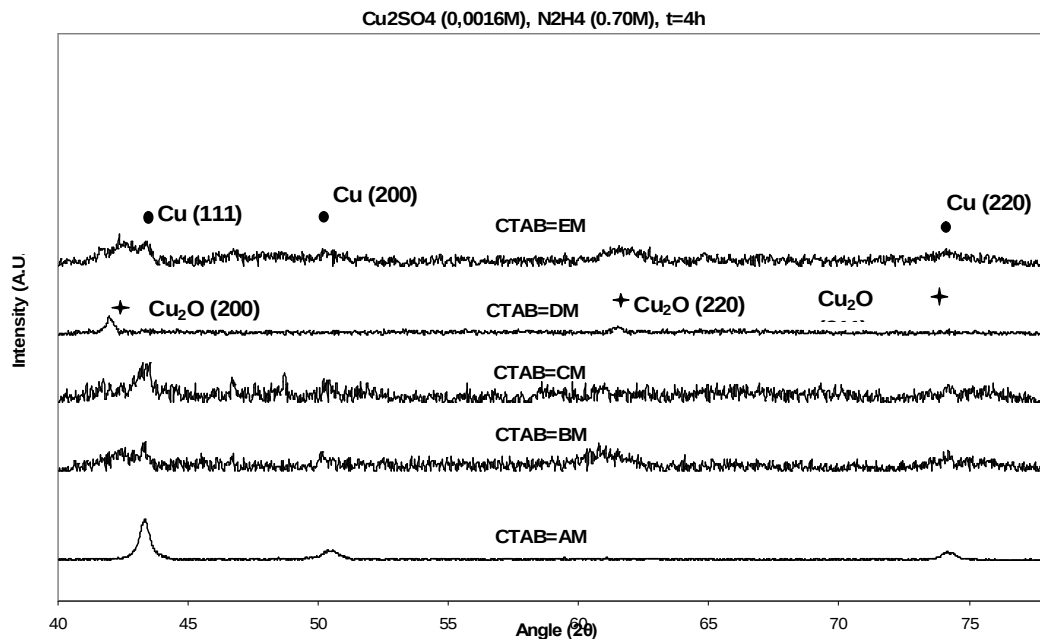


Figure 37. XRD patterns of recovered solids at different CTAB concentration, Cu concentration was 0.0016M, and Hydrazine concentration was 0.70M, total time was 4 hours, AM=0.00052M, BM=0.00260M, CM=0,00520M, DM=0,00780M, EM=0,01040M.

The above discussed results confirmed the possibility of synthesizing Cu nanoparticles in aqueous media by a suitable control of the reducing conditions. Moreover, the use of surfactants will lead to very stable suspensions making the removal of nanoparticles and the preparation of the corresponding nanofluids a very complicated task.

4.1.1.2 UV-vis measurements

Figure 38 shows the UV-vis spectra for copper nanoparticles suspended in ethanol. The nanoparticles were synthesized from starting 0.016M Cu and various concentrations of hydrazine ranging from 0.13M up to 0.70M. As seen, all spectra displayed a surface plasmon (SP) resonance band at around 600 nm that can be attributed to Cu nanoparticles [10, 22, 27, 25, 28, 52, 63 and 64]. The band broadening can be explained by the polydispersity in particle size.

Galkowski *et al.* observed that a SP band centered on 600nm appeared when the Cu nanoparticles have 100nm in size [65]. This estimation in size is in disagreement with our results; although in our case the SP band also appears at 600nm (figure 38) the crystallite size estimated by XRD was 20nm. However, to have a more complete idea of the situation in our system, it is necessary to take into account that the presence and location of the surface plasmon band is strongly dependent on the size, shape and state of aggregation of the nanoparticles during UV-vis measurements (see section 2.5.5). We might have produced aggregated nanoparticles which would behave as bigger ones during UV-vis measurements, a fact that is not discriminated by XRD estimations of the average crystallite size.

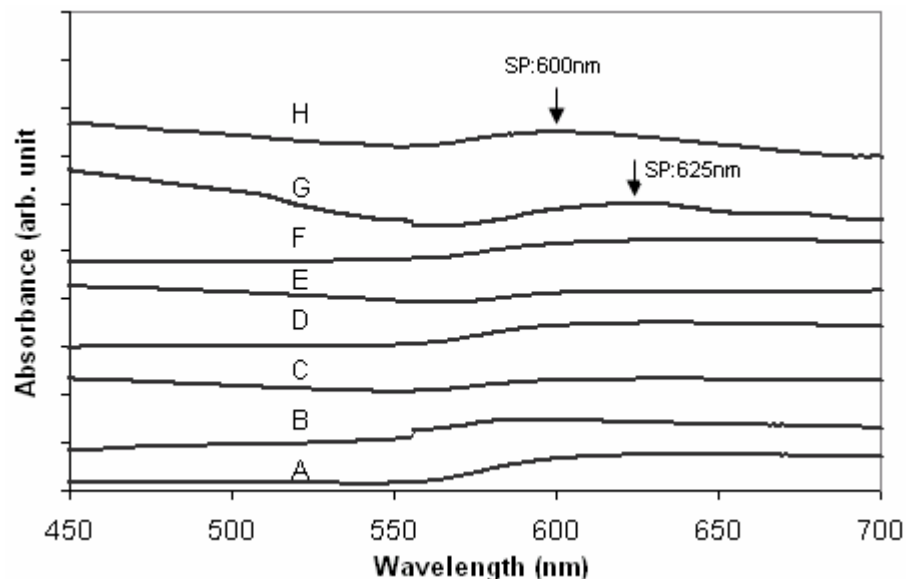


Figure 38. UV/VIS absorption spectrum of copper nanoparticles synthesized in aqueous solution and suspended in ethanol. The concentration in all the samples for copper solution is 0.0016M and for hydrazine: : (A)0.13M, 9h, (B) 0.18M, 7h, (C)0.24M, 6h, (D) 0.30M, 4h, (E) 0.35M, 3h, (F) 0.47M, 2h, (G)0.65M, 1h, (H) 0.70M, 0.5h.

4.1.1.3 Morphological analysis

TEM and SEM images of copper nanoparticles synthesized in hydrazine aqueous solutions are shown in figures 39 and 40. The synthesis conditions were 0.064M Cu and N_2H_4 0.059 M (figure 39) and 0.016M Cu and N_2H_4 0.70 M (figure 37). Although strongly aggregated, the images evidenced the nanocrystalline nature of the particles and the decrease in size due to improvement in reaction velocity caused by a large concentration of hydrazine: the particle size went down to below 20nm when 0.70M hydrazine was used.. This trend is in good agreement with data provided by XRD analyses presented in section 4.111 of this thesis.

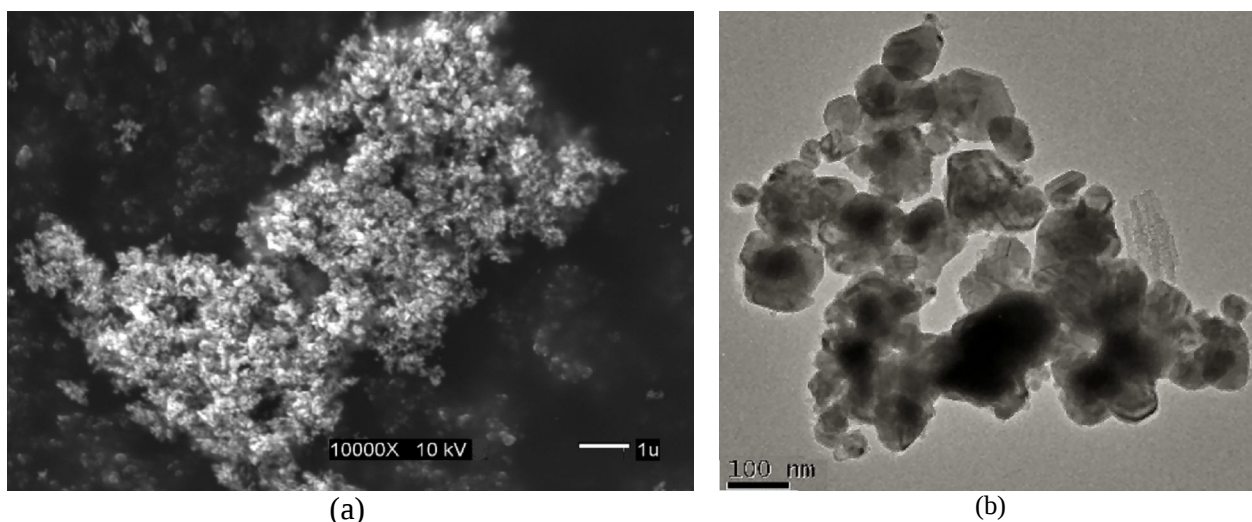


Figure 39. SEM (a) and TEM (b) pictures of copper nanoparticles synthesized using 0,064 M copper solution and 0,059 M of hydrazine solution.

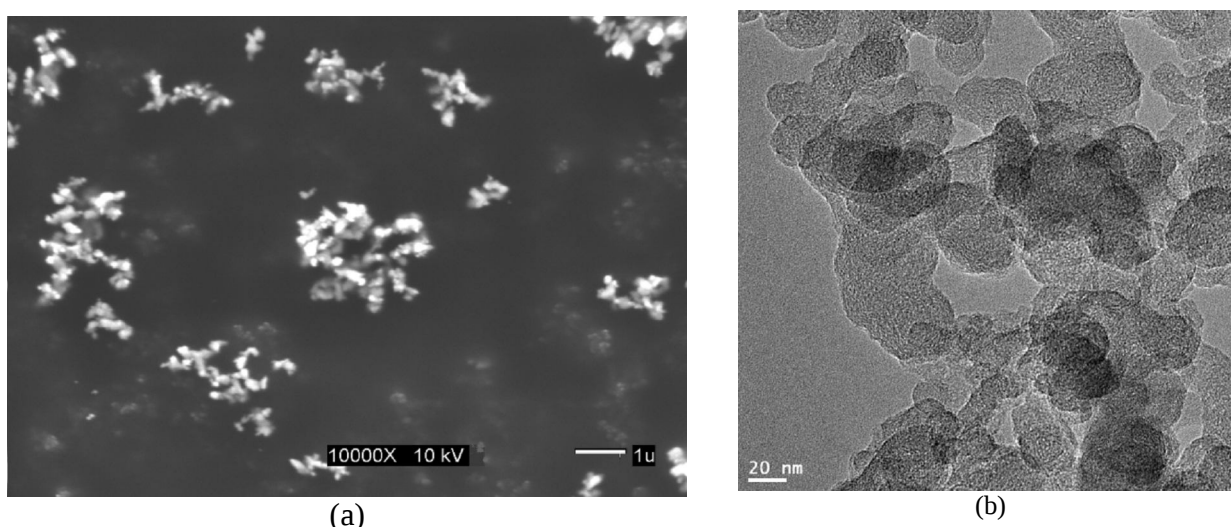


Figure 40. SEM (a) and TEM (b) pictures of copper nanoparticles synthesized using 0,016 M copper solution and 0,70 M of hydrazine solution.

4.1.2 Cu(II) Reduction in Ethylene glycol

Cu(II) species were also reduced into elemental copper in ethylene glycol solutions under boiling conditions. The following parameters were evaluated as a function of the reaction

time: heating intensity (in terms of ‘mantle heat power’), Cu concentration, NaOH/Cu mole ratio and PVP concentration.

4.1.2.1 Structural characterization by x-ray diffraction

4.1.2.1.1 Effect of reaction time

Figures 41 and 42 shows typical XRD patterns for the solids produced after reduction of 0.0016M Cu(II) and 0.0064M Cu(II) in boiling ethylene glycol, where the reaction time varied from 10 minutes up to one hour. The reaction was carried out at a 50% of in total power for a mantle heater. The formation of elemental copper was a very fast process; only 20 minutes were needed to form copper, in contrast with the more than 12 hours required in hydrazine solutions in the initial tests. The XRD patterns of figure 46 clearly show the evolution of the copper-forming reaction. First, Cu(I) oxide coexisted with elemental Cu. After 20 minutes all peaks corresponding to the cuprous oxide were not detected and only sharp peaks of elemental Cu were observed. Again, the mechanism of Cu formation should involve the partial reduction of Cu(II) into Cu(I) species, followed by re-dissolution of the Cu(I) oxide and subsequent reduction of Cu(I) into zero-valence Cu. When the concentration of Cu ions was 0.0064M, the formation of elemental Cu was somehow delayed. The XRD pattern for the solids produced after 10 minutes of reaction confirms the exclusive formation of intermediate Cu₂O, with no evidence of Cu formation as observed at lower starting Cu concentration. Our preliminary data suggests the kinetic enhancement of Cu formation in EG when compared to water. It can be a consequence not only of the stronger reducing power of ethylene glycol solutions but also, the higher temperatures used for synthesis in

polyol solutions ($\sim 197^\circ\text{C}$). The variation in the average crystallite size during the formation of elemental Cu will be discussed in the next section of this thesis.

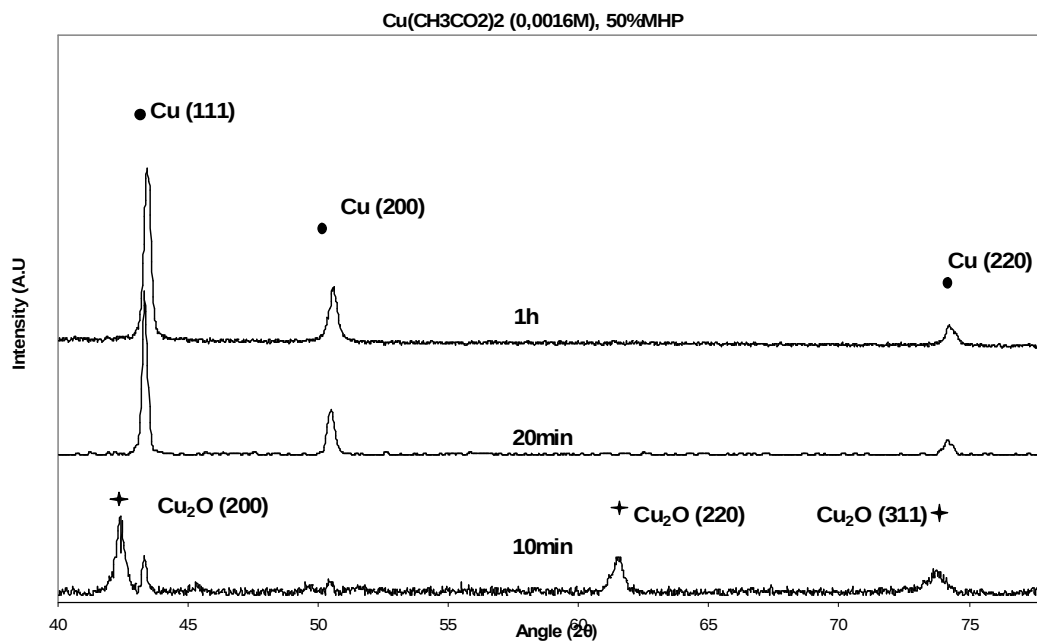


Figure 41. XRD patterns of powders synthesized at different reaction times. Reactants concentrations were 0.0016M Cu and 50% in mantle heat power

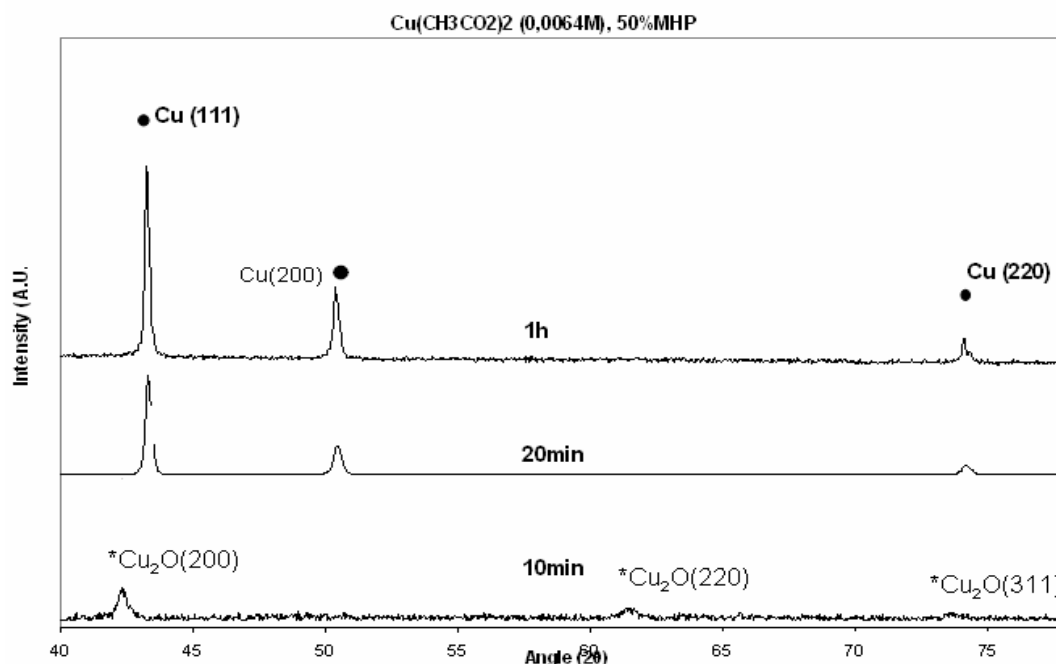


Figure 42. XRD patterns of powders synthesized at different reaction times. Reactants concentrations were 0.0064M Cu and 50% in mantle heat power

4.1.2.1.2 Effect of Cu(II) concentration

A decrease in the concentration of Cu ions in ethylene glycol, while keeping constant the reaction volume, actually represents an increase of the reducing agent/Cu(II) ratio. In other words, the lower the concentration of Cu(II) ions the greater the availability of the reducing agent ethylene glycol and hence, the stronger the reducing conditions in the boiling polyol system. Based on this consideration, two concentrations of copper solution were evaluated, 0.0016M and 0.0064M, which correspond to the highest and lowest concentrations evaluated in copper reduction using hydrazine solutions.

A stronger reducing condition would lead to a faster formation of reduced species, i.e. cuprous oxide and elemental copper. Figure 43 show the XRD patterns for the solids produced at 0.0016M and 0.0064M Cu, respectively, after 10 minutes of reaction. Solids were produced under a 50% heat power condition. As expected, a decrease in copper concentration accelerated the formation of zero-valence copper. Elemental copper co-existed with Cu_2O when the solids were synthesized from a 0.0016M Cu solution; whereas only Cu_2O was formed from starting 0.0064M Cu solution. The corresponding average crystallite sizes are 38.7nm and 32.8nm for 0,0064M Cu and 0,0016M Cu solutions for 1 hour of reaction and after 20 minutes of reaction receptively, and 26.2 nm after 20 minutes of reaction for 0,0016M Cu solutions, the corresponding lattice parameter was estimated at 3.614 Å, which is good agreement with the bulk value of 3.615 Å.

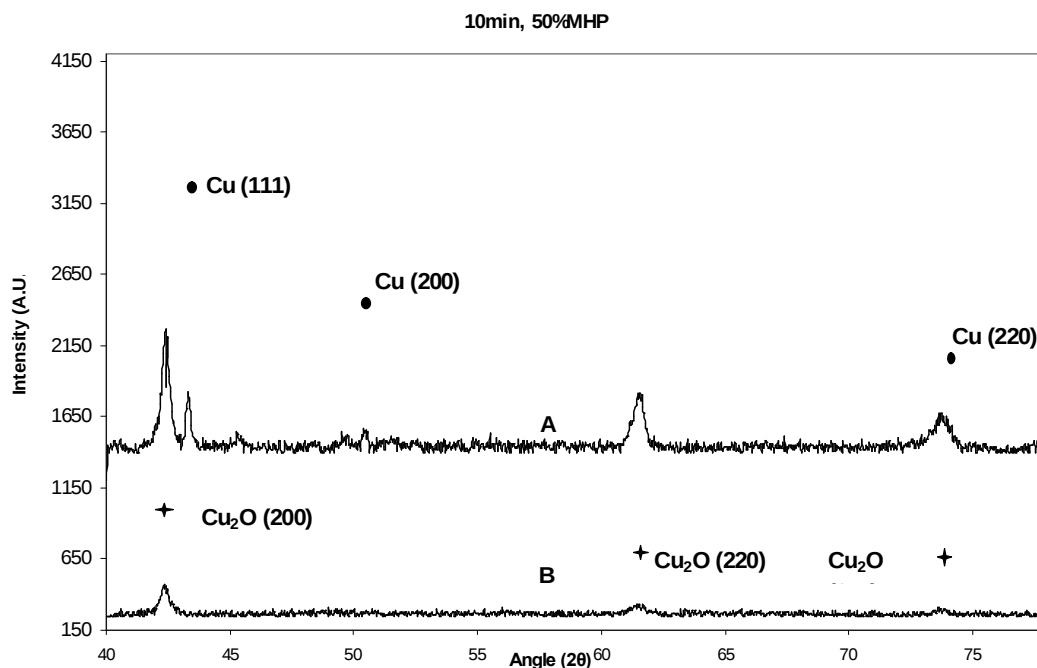


Figure 43. XRD patterns of powders synthesized at different copper concentrations, A: 0,0016M, B: 0,0064M, 10 minutes of reaction and 50% of mantle heat power

On the above basis, the following experiments were conducted using a starting copper concentration of 0,0016M.

4.1.2.1.3 Mantle ‘heat power’ effect

The mantle heater used in our synthesis experiments allows a control of the ‘heating intensity’ by controlling the ‘heat power’ of the set-up (50% or 100% of total available power for heating). Therefore, a couple of experiments were carried out at those two different heating powers and using a 0.0016M Cu solution. The reaction time was kept constant at 10 minutes. Figure 44 shows the XRD patterns for the corresponding solids. Evidently, the more intense heating condition provided by the ‘100% heat power’ accelerated the exclusive formation of elemental Cu. A more intense heating condition accelerates the intermediate reactions (alcoxide precursor precipitation, precursor-dissolution and reduction of Cu species) involved with the formation of elemental copper.

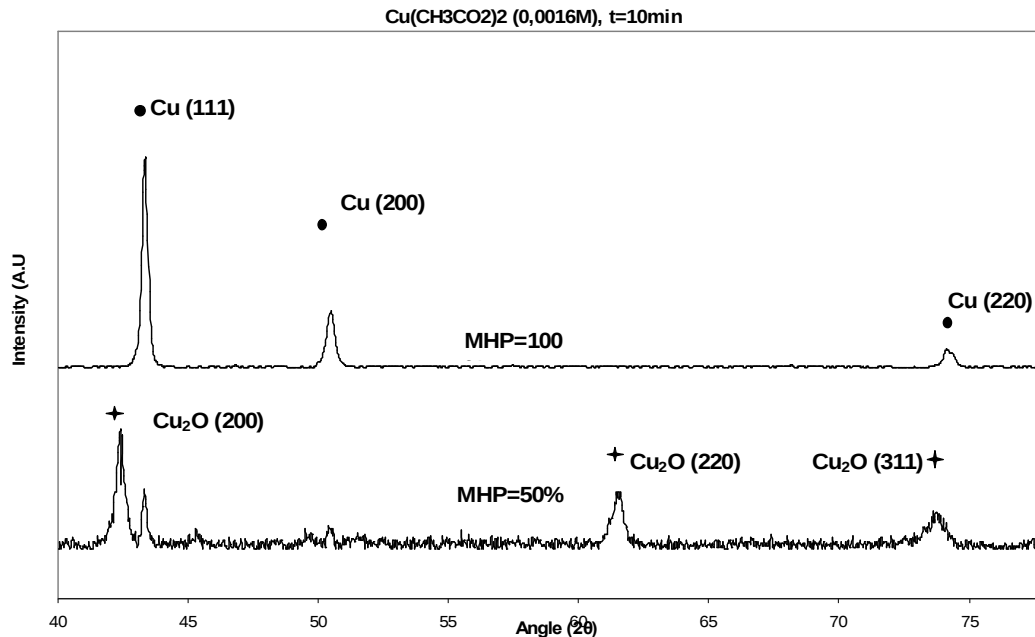


Figure 44. XRD patterns of powders synthesized at different mantle heat power. Cu concentration was 0.0016M

The average crystallite obtained for 0,0016M of copper solution and 100% of mantle heating power corresponds to 25nm that is slightly below the 26,2nm obtained when 50% MHP was used. Considering the above discussion, 100 % of mantle heat power was selected for the forthcoming experiments.

4.1.2.1.4 Effect of the NaOH/Cu mole ratio, 'R'

XRD patterns in figure 45 correspond to the solids produced in ethylene glycol at different NaOH/Cu mole ratios, R'. The initial Cu(II) concentration was 0.0016M and the patterns corresponds to those reaction times at which the formation of elemental copper was realized. In short, the presence of NaOH accelerated the formation of elemental Cu; the reaction time was shortened from 10 minutes to 30 s when the 'R' values varied from 0, i.e. no NaOH, to

50. The corresponding average crystallite size decreased from 25nm to 21nm. The excess of NaOH enhances the reducing conditions in the polyol media and/or accelerates the dissolution of any intermediate phase under strongly alkaline conditions, for example, as the NaOH catalyzes the conversion of ethylene glycol to acetaldehyde (see equation 17 in page 23), and as the acetaldehyde acts as reduction agent for cuprous oxide, (see equation 16, the same page), an enhancement of the nucleation rate, and hence the reduction in crystal size for copper nanoparticles, could be expected. Table 13 summarizes the observed variation in the average crystallite size. The above behavior for NaOH solutions in polyol synthesis is in agreement with related works [62].

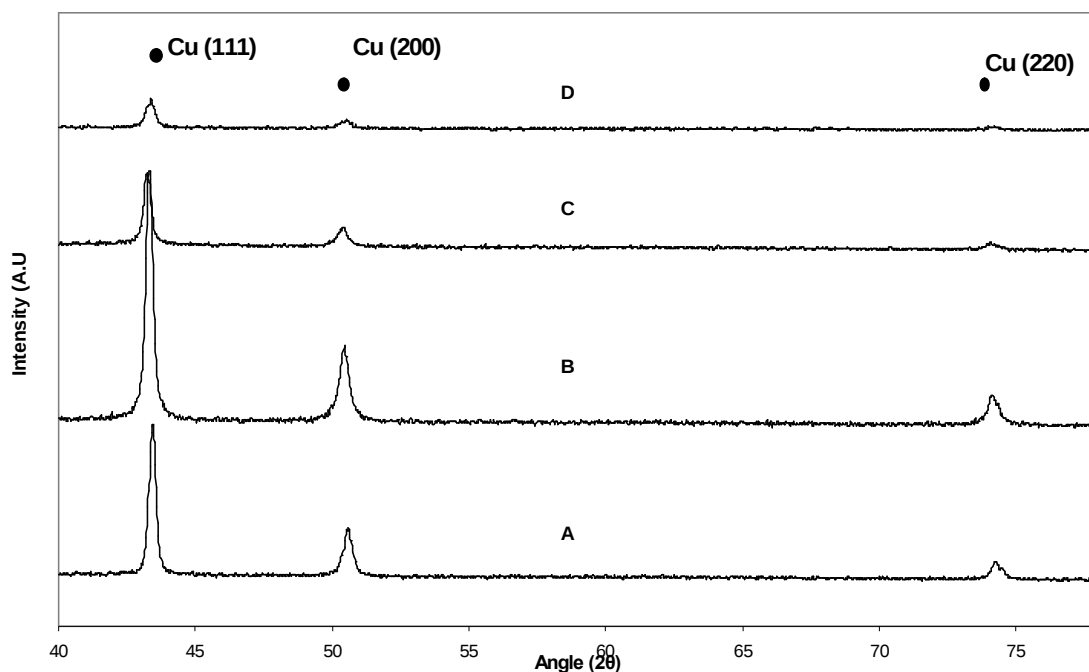


Figure 45. XRD patterns of Cu particles synthesized in ethylene glycol at NaOH/Cu mole ratio, 'R' and time of 0,20min (A); 1, 20 min (B), 10, 30s (C) and 50,30s (D). The initial Cu concentration was 0.0016M.

Table 13. Crystallite size as a function of NaOH/Cu mole ratio, ('R'), in polyol reduction for copper.

NaOH/Cu mole ratio 'R'	Average crystallite size (nm)
0	25,0
1	24,8
10	24,1
50	21,2

Figure 46 shows that high 'R' values accelerated the Cu formation. The time required to produce elemental Cu decreased from 10 minutes ('R' = 0) down to 30 seconds ('R' = 50).

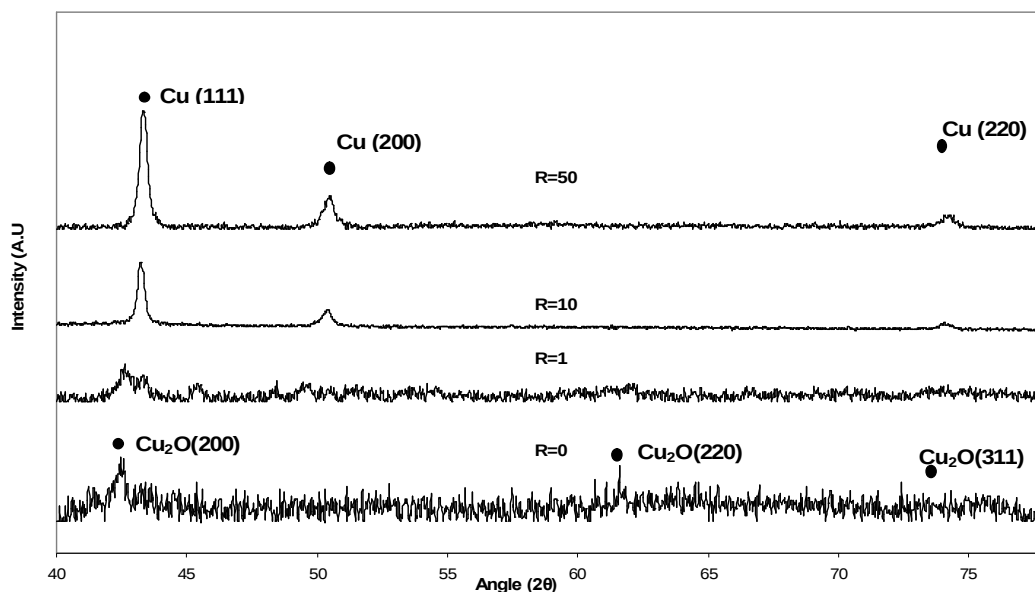


Figure 46. XRD patterns of Cu particles synthesized in ethylene glycol at various R ratios and reaction times: R= 0, 10min, R= 1, 30s, R= 10, 30s, R= 50, 30s respectively. The initial Cu concentration was 0.0016M.

Considering that the addition of NaOH accelerates the reaction and decrease the crystallite size, a NaOH/Cu mole ratio of 50 was selected for the following experiments.

4.1.2.1.5 Effect of Polyvinylpyrrolidone (PVP) addition

So far, we have determined the most suitable conditions for the synthesis of Cu nanoparticles: 30 seconds of reaction, 'R'= 50, 100% mantle heat power and 0,0016M of copper solution. Then, the effect of PVP addition on the Cu forming reaction rate and corresponding average crystallite size will be evaluated. PVP is a soluble polymer and its presence can help to minimize aggregation of nanoparticles and restrict particle growth.

Figure 47 shows the XRD patterns of the solids produced from a 0.0016M Cu solution in EG and various concentrations of PVP. The reaction time was 30 seconds in all cases. The peak broadening observed in the patterns at higher PVP concentrations suggests the decrease in crystallite size. The corresponding average crystallite sizes were estimated at 20.7nm and 12.7nm for Cu synthesized in presence of $1 \cdot 10^{-7}$ M and $5 \cdot 10^{-7}$ M PVP solutions. Table 14 summarizes the variation on the average crystallite size with PVP concentration. The PVP proved to be an effective growth inhibitor agent; in fact, the formation of Cu was not delayed by the presence of PVP. The main concern with this Cu production route relies on the extremely high stability of the nanoparticles suspensions, which makes their removal very complicated. It was necessary to dry the suspension under vacuum conditions to recover the powders and characterize them. Evidently, this suspension stability makes the preparation of the corresponding nanofluid difficult. Nevertheless, the development of a faster nanoparticles removal process will be investigated in future research.

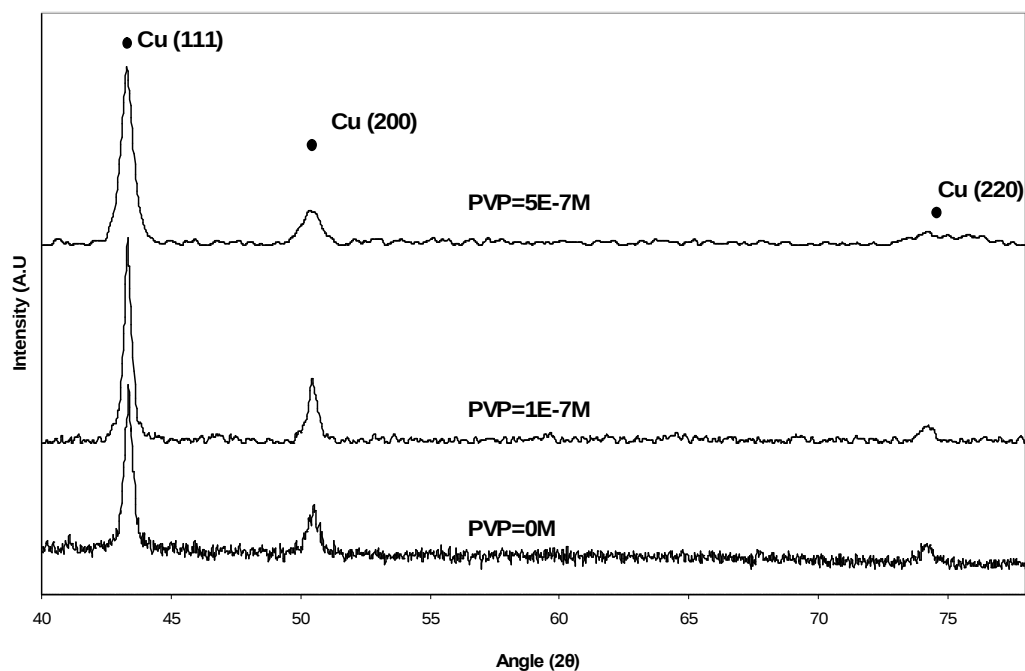


Figure 47. XRD patterns of recovered solids at different PVP concentration, Cu concentration was 0.0016M, , total time was 30 seconds.

Table 14. Crystallite size as function of PVP concentration in polyol reduction for copper. Other synthesis conditions were 0,0016M copper solution, 'R'=50, 100% mantle heat power

PVP Concentration	Average crystallite size (nm)
0	21,2
1 E-7M	20,7
5 E-7M	12,7

4.1.2.2 UV-vis measurements

Figure 48 shows the UV-vis spectra of the Cu nanoparticles synthesized in EG at different conditions and suspended in ethanol. As seen, the SP band was more clearly observed in those samples produced under optimum conditions (spectra 'E' and 'F'). This behavior is in concordance with XRD information. The spectra displayed a SP resonance band at around 590nm, which is also typical of Cu particles. Mott et al. observed the SP band at ~600nm [65]

when $\sim 100\text{nm}$ Cu nanoparticles were suspended in hexane. As known, the exact position of the SP may depend on several factors including particle size, shape, solvent type and capping agent, if any. Furthermore, the observed narrowing of the SP band in the solid produced at $R = 50$ suggests a lower polydispersity in size.

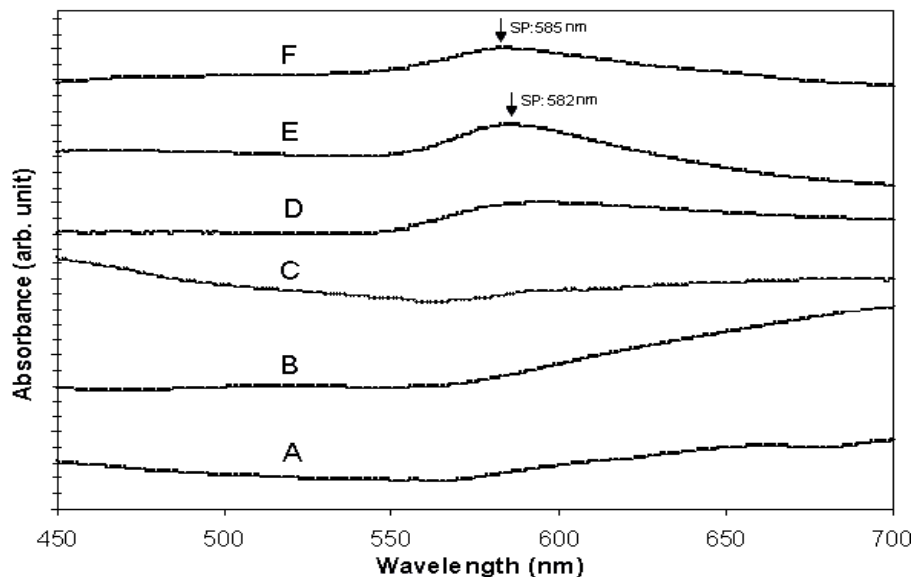


Figure 48. UV/VIS absorption spectrum of copper nanoparticles synthesized in ethylene glycol and suspended in ethanol. (A) 0,0064M Cu, 50%MHP, (B) 0,0016M Cu, 50%MHP, (C) 0,0016M Cu, 100%MHP, (D) 0,0016M Cu, 100%MHP, ' R' '=1, (E) 0,0016M Cu, 100%MHP, ' R' '=10, (F) 0,0016M Cu, 100%MHP, ' R' '=50.

4.1.2.3 Morphological analysis

Figure 49 shows TEM micrographs for the solid synthesized in EG. The production of nanometric size and less aggregated Cu particles, of around 20nm in diameter, is clearly observed. It must also be emphasized that observed crystal sizes are in good agreement with XRD estimation that is suggestive of the formation of single crystals.

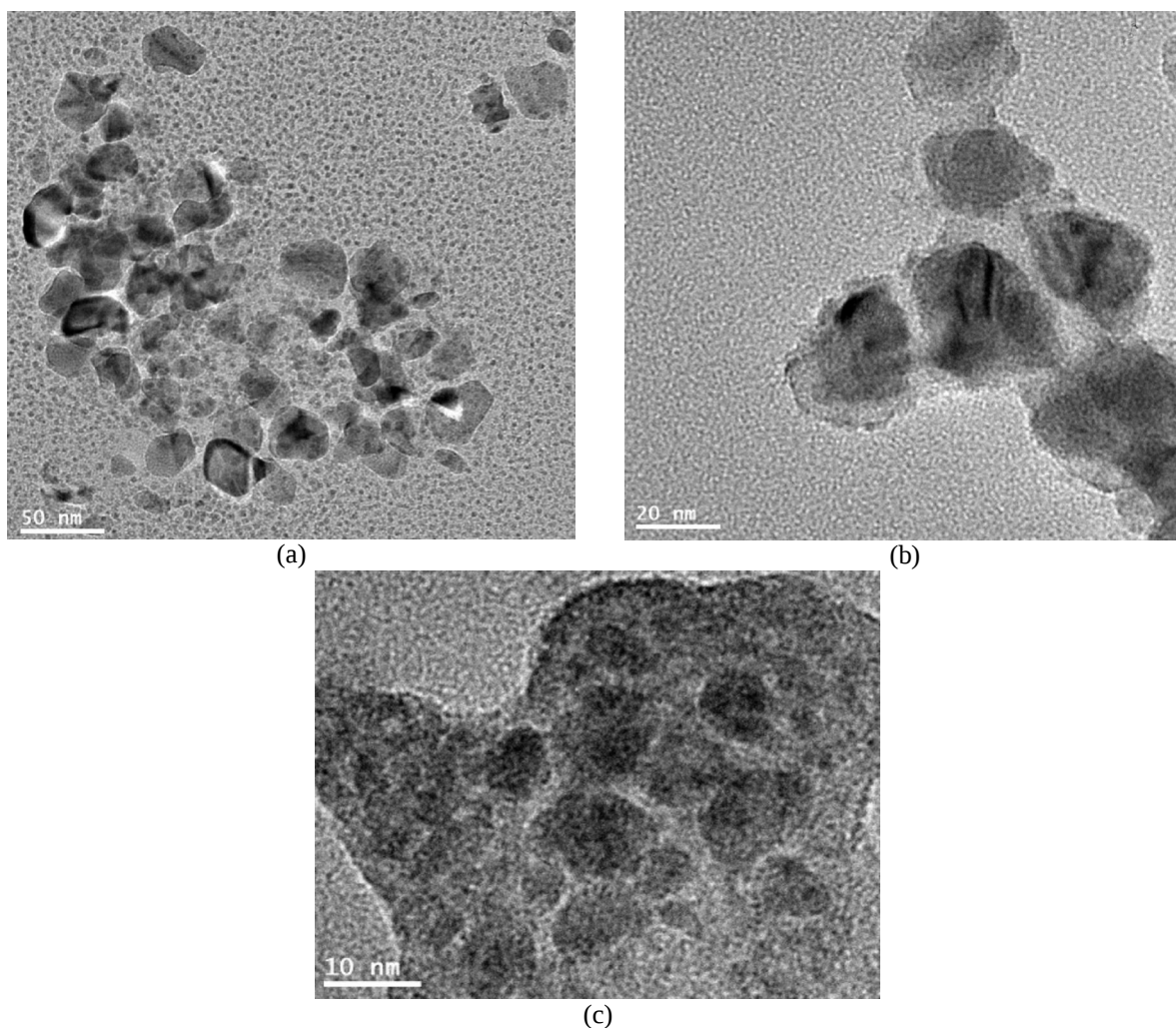


Figure 49. TEM images of Cu nanoparticles synthesized in EG using a) 0,0064M Cu, $t=20$ min b) 0,0016M Cu, $R'=10$, $t=30$ s and c) 0,0016M Cu, $R'=10$, 5E-7M PVP. The reaction time was five minutes.

So far, our research work has demonstrated the viability in synthesizing Cu nanoparticles in the 10nm-20nm range by using hydrazine or ethylene glycol. Our results suggested that polyol technique represented a more convenient route for nanoparticle synthesis because the possibility of producing nanosize non-aggregated single crystals at extremely short reaction times.

4.2 Nanofluid preparation and thermal conductivity measurements

4.2.1 XRD characterization

In order to assure the stability of the nanofluid at least during the measurements of the thermal conductivity, Cu samples were suspended in EG and strongly sonicated for 7 hours. In order to confirm that the suspended nanoparticles did not suffer any chemical (oxidation) change during the sonication process, the nanoparticles were recovered by centrifugation and submitted for XRD analyses. Figure 50 shows the XRD pattern for solid recovered after sonication in EG. All peaks corresponded to elemental Cu, which suggests the chemical stability of the nanoparticles even during such an intensive sonication pre-treatment. The estimated average crystallite size was 11,7 nm that is slightly below the size estimated by XRD for the samples without intensive sonication, (that correspond to 21.2nm). The reduction in size suggests that sonication will help to decrease nanoparticle size even further. The mechanisms involved with this change in size are still unclear, although some rupture of the crystals or partial dissolution in EG during sonication could explain the observed change in size. The suspensions prepared by following this intensive sonication approach were quite stable; no settling of nanoparticles was observed nor change in the color of suspensions were detected even after 3 months of the nanofluid preparation.

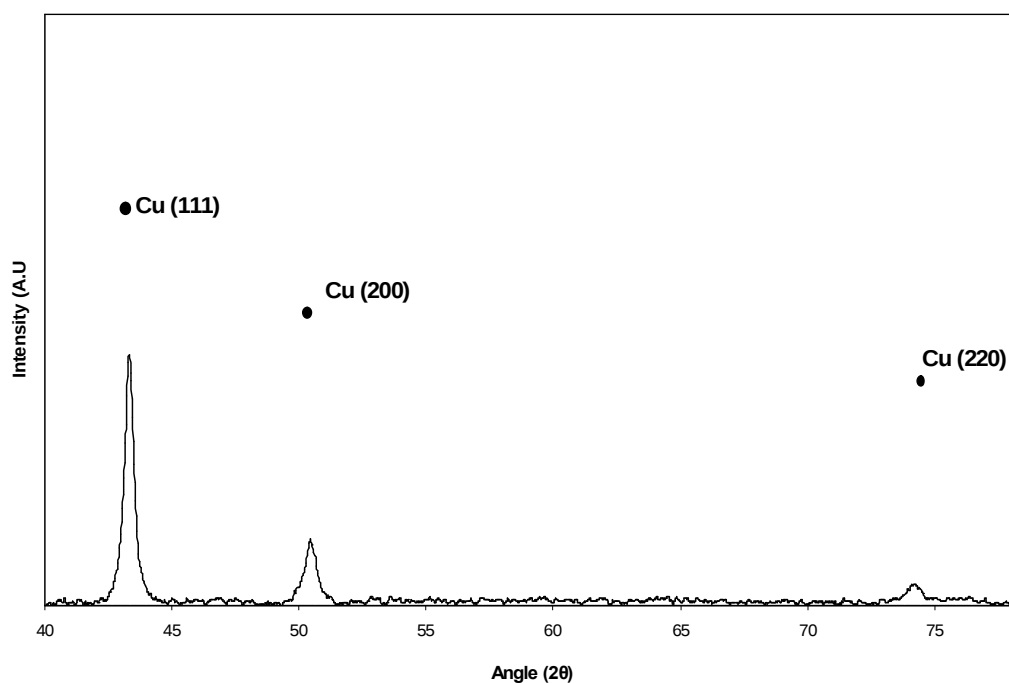


Figure 50. XRD patterns of recovered solids after intensive sonication treatment.

4.2.2 UV VIS characterization

Copper nanoparticles synthesized in aqueous (hydrazine reduction) and non-aqueous (polyol reduction) media, (see figures 51 and 52), were suspended in ethylene glycol and treated with sonication. Copper nanoparticles were treated by 0.001M HCl solution in ethanol prior to their sonication. The volumetric % of the nanocrystals in the fluid was estimated at 0.001 %, 0,05%, 0,003% , 0,020% and 0,080%, volumetric concentration correspond to the copper, ethylene glycol volume ratio multiplied by 100, the copper volume is determined weighting a specific copper nanoparticle sample and multiplied by copper density. In order to promote the nanofluid stability against sedimentation, the suspension was intensively ultrasonicated for 7 hours. The final suspension exhibited an orange tone and showed no evidence of

settling of particles even after 96 hours. The UV-vis spectra were collected during 25 minutes at 5 minutes interval to determine the stability of the suspension.

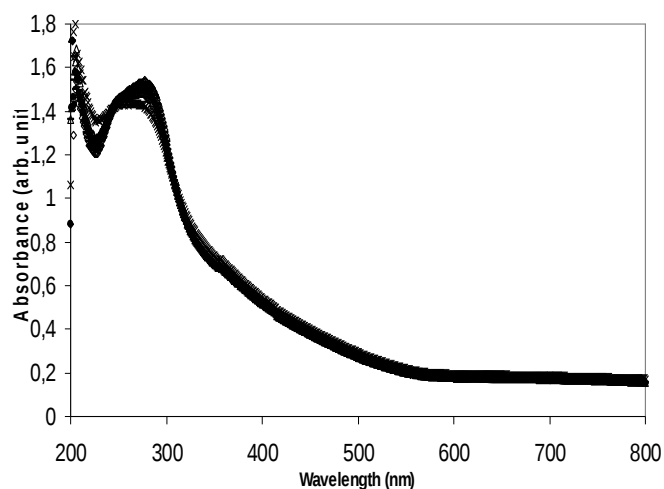


Figure 51. UV/VIS absorption spectra of Cu nanoparticles synthesized and suspended in ethylene glycol and sonicated by 7 hours. The initial Cu concentration and 'R' were 0.0016M and 50, respectively.

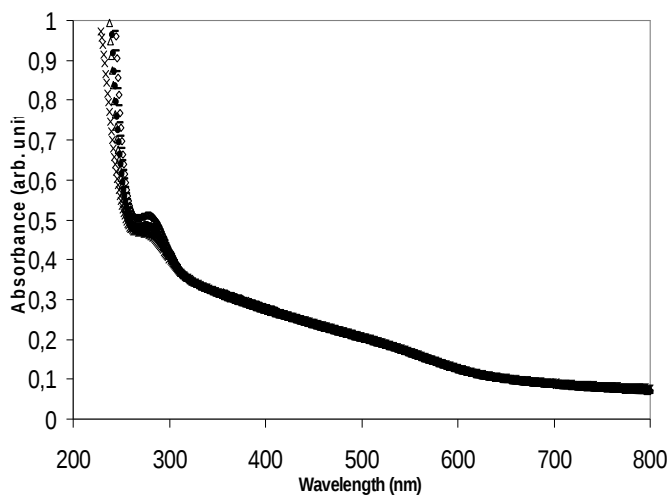


Figure 52. UV/VIS absorption spectra of Cu nanoparticles synthesized in 0.70M of hydrazine and suspended in ethylene glycol and sonicated by 7 hours. The initial Cu concentration was 0.0016M.

As figures 51 and 52 show, the surface plasmon (SP) resonance band was centered on 280nm and no remarkable shifting was observed in the measurement period. This fact may suggest the stability of the suspension at least during the 25 minutes period of data collection. Nevertheless, the position of the SP band was blue-shifted with respect to the SP position shown in figures 51 and 52. On the consideration that no dissolution of Cu nanoparticles could have taken place in ethylene glycol media, this blue shift can be a consequence of the reduction in the nanoparticles size (fragmentation) by intensive ultrasonication. The position of the SP resonance band is in agreement with other reports where the size of Cu nanoparticles was in the 2-4nm range [11, 12].

Figure 53 shows the UV-vis spectra of Cu nanoparticles synthesized in EG, treated by 0.001M HCl solution in ethanol and suspended in fresh ethylene glycol without sonication treatment. The volumetric load of the nanocrystals in the fluid was estimated at 0.001 %, 0,05%, 0,003% , 0,020% and 0,080%. The UV-vis spectra's were collected during 25 minutes at 5 minute intervals. As seen, the SP resonance band was centered on 587nm and no remarkable shifting was observed along the measurement period. This fact may suggest the stability of the suspension at least during the 25 minutes-period of data collection.

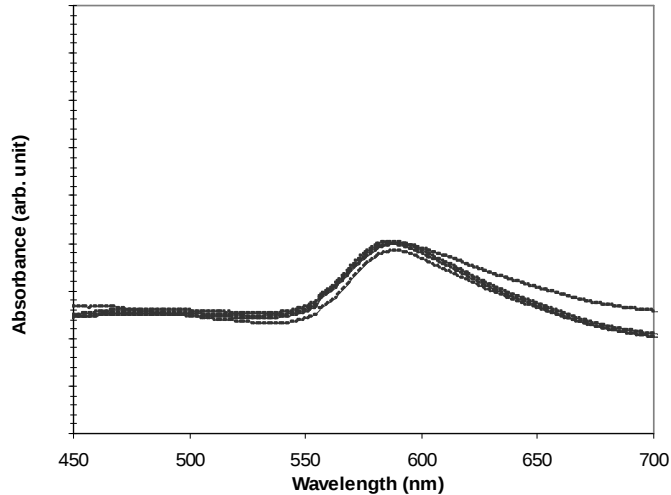


Figure 53. UV/VIS absorption spectra of Cu nanoparticles synthesized and suspended in ethylene glycol. The initial Cu concentration and 'R' were 0.0016M and 50, respectively.

4.2.3 Morphological analysis of suspended Cu nanoparticles.

Figure 54 shows TEM micrographs for the Cu nanoparticles that were treated by intensive ultrasonication in EG. The image suggests a particle size of around 5nm, which is in very good agreement with the values estimated from XRD and UV-vis measurements. The intensive ultrasonication might have fractured Cu nanocrystals and/or favored their chemical dissolution in EG during the preparation of the nanofluid.

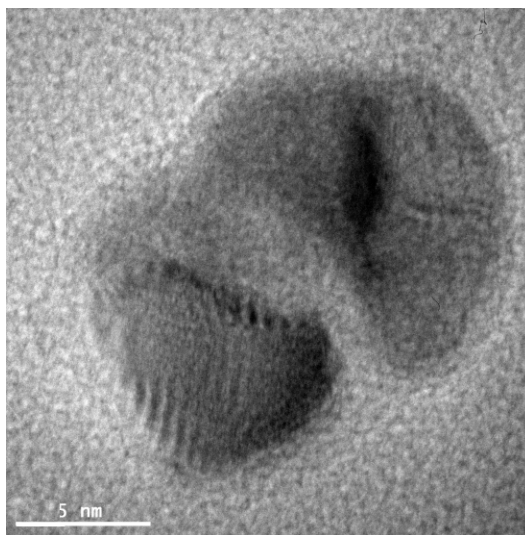


Figure 54. TEM images of Cu nanoparticles synthesized in EG using 0,0016M Cu, $R'=10$, $t= 30s$ and ultrasonicated for 7 hours

4.2.4 Nanofluids thermal conductivity measurements

The ratios between thermal conductivity for nanofluid and thermal conductivity for the base fluid (EG), $K = K_{eff}/K_f$, for different volumetric loads of nanoparticles were measured and presented in Table 15 and figure 55. All measurements were carried out at 23°C. The constant 'C' of equation 29 (page 38) included the unavoidable experimental error associated with measurements. Accordingly, the use of the ratio $K = K_{eff}/K_f$, instead of the absolute values of the thermal conductivity was preferred. 'Treated' and 'non-treated' samples are used to refer to the suspension prepared under intensive and normal ultrasonication conditions, respectively.

As observed, the variation in the ratio K_{eff}/K_f was negligible for much diluted suspensions in the range between 0.001 v/v% and 0.08 v/v %; all measured data was within the experimental error range. It must be recalled that the crystal size in 'treated samples' are

much smaller than in ‘non—treated’ ones. In the case of ‘non treated samples’ the average crystallite size of suspended particles was around 20nm. In this case, the increment in thermal conductivity was detected in nanofluids with a volumetric load as low as 0.08 v/v/ %. Afterwards, the ‘K’ ratio exhibited a systematic and rising trend with increase of the volumetric load. The nanofluid exhibited an increase of up to 32% in ‘K’ when the volumetric load was as low as 7.5 v/v%.

Table 15. Thermal conductivity measurement for treated and not treated nanofluids.

	Sample	K_{eff}/K_f :	Error calculated based in Standard deviation (3σ)
treated	0,001 %V/V Cu_EG	1.01	0.02
	0,003 %V/V Cu_EG	1.00	0.02
	0,020 %V/V Cu_EG	1.01	0.01
	0,080 %V/V Cu_EG	1.00	0.02
Non treated	0,001 %V/V Cu_EG	0.99	0.02
	0,003 %V/V Cu_EG	0.98	0.02
	0,020 %V/V Cu_EG	1.00	0.02
	0,080 %V/V Cu_EG	1.01	0.01
	0.80% V/V Cu_EG	1.02	0.02
	1.50% V/V Cu_EG	1.04	0.01
	3.00% V/V Cu_EG	1.16	0.03
	3.50% V/V Cu_EG	1.21	0.02
	5% V/V Cu_EG	1.26	0.02
	7.50% V/V Cu_EG	1.32	0.03

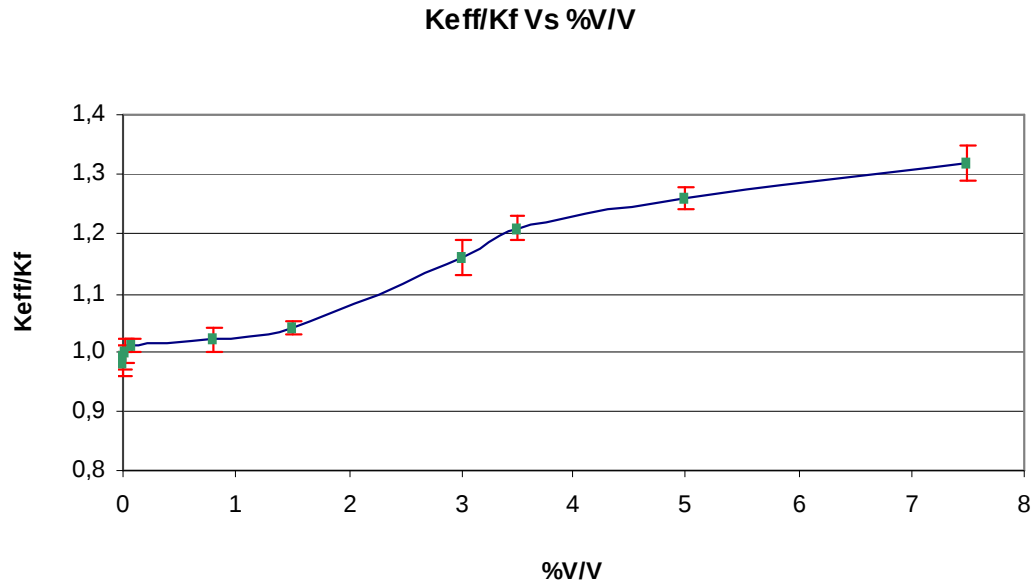


Figure 55. Variation in relative thermal conductivity respect to volumetric load of Cu nanoparticles v/v %. The Cu nanoparticles averaged 21.2nm and were synthesized in ethylene glycol. Samples were not pre-treated by intensive ultrasonication ('non-treated')

Choi *et al.* [66], reported an increase in thermal conductivity of 40% of 10nm-Cu bearing nanofluids at a 0.3 vol% in ethylene glycol. The discrepancy with our results can be explained by the difference between the average particle size that was used in these two studies: 10nm for Choi's and 20nm in ours. The fact that Choi's report involved the use of an stabilizing agent in the nanofluid should also account for our differences. Therefore, a more detailed study evaluating the thermal conductivity with Cu particles of different sizes and types of stabilizing agents effects should be considered in future research. Furthermore, the direct comparison between our results with others must also consider probable discrepancies between the sensitivity in the set-ups used for the thermal conductivity measurements. Our work identified several deficiencies and critical points in the design based in the hot-wire technique. These deficiencies, which were addressed and overcome in our work, can strongly affect the obtained values, making a review of reported data advisable.

Section 2.6 included the description of available thermal conductivity models for stable suspensions. Also, a mechanistic discussion on factors affecting these measurements was presented. On that basis, there is no valid model to explain the observed increase in thermal conductivity in nanofluids. At present, and based on our own results, the promoting effect of the volumetric load of Cu nanoparticles on the thermal conductivity of the nanofluid has been verified.

Considering the Maxwell's model, (equation 25 in page 33), an approximate relative thermal conductivity can be determined from 32.

$$\frac{k_{eff}}{k_b} = \frac{k_p + 2k_b + 2(k_p - k_b)\phi}{k_p + 2k_b - (k_p - k_b)\phi} \quad (32)$$

If we replace the volumetric concentration of 7.5%, ($\phi = 0,075$) in the above equation, a thermal conductivity for copper of 401 w/(m*K) and for ethylene glycol of 0.252 w/(m*K) can be calculated. These values make a 'K' ratio of 1.24, which is not in agreement with our result (1.32, in table 15). This comparative calculation suggests that the Maxwell equation would under estimate the thermal conductivity value; the observed discrepancy of 6.5% is above the experimental error in our experiments (near 2%).

The enhancement in thermal conductivity is strongly dependent on volumetric concentration of the nanoparticles in the fluid. We can estimate an approximate value for inter-particle

distance, λ , as function of size and volumetric concentration. Equation 33 can be used assuming spherical nanoparticles of equal size,.

$$\lambda = r * \sqrt[3]{\frac{4 * \pi}{3 * x_{v/v}}} \quad (33)$$

Where 'r' is the radius of the nanoparticles and $x_{v/v}$ is the volumetric fraction, ($x_{v/v} = \%v/100$).

The inter-particle distance measured with respect to nanoparticles diameter, ($\Gamma/(2 * r)$), can be derived from equation 33 leading to equation 34.

$$\Gamma = \sqrt[3]{\frac{\pi}{6 * x_{v/v}}} \quad (34)$$

The true diameter length, (Γ^*), between nanoparticles can be obtained after considering the volume of the nanoparticles:

$$\Gamma^* = \sqrt[3]{\frac{\pi}{6 * x_{v/v}}} - 1 \quad (35)$$

Equation 35 indicates that when the volumetric concentration is increased the diameter length between nanoparticles is decreased. Γ^* represents the number of nanoparticle diameters between the surface of two adjacent nanoparticles. Table 16 shows the true inter particle length, calculated from previous equations, as function of volumetric concentration of nanoparticles in the fluid.

Table 16. True diameter length as function of volumetric concentration

%v/v	true diameter length (Γ^*)
0,001	36,4110193
0,003	24,939352
0,02	12,7823373
0,08	7,68232846
0,8	3,02997989
1,5	2,26815356
3,0	1,5939352
3,5	1,46401601
5,0	1,18780968
7,5	0,9112278

As expected, the increase in the volumetric concentration was conducive to a decrease in inter particle length. This inter particle length could be related to the observed enhancement of the thermal conductivity and must be considered, at least in part, in any further effort on modelling the thermal behaviour of nanofluids. For instance, a true diameter length of 0,91 is calculated for 7.5% v/v and 10 nm copper nanoparticles. It means that the surfaces between two neighbor nanoparticles are separated by 9.1 nm. This value represents a drastic decrease in the inter particle distance when compared to 19.9nm calculated for 21.2nm particles at similar volumetric load (as synthesized in our work). Under these conditions, the increase in thermal conductivity by considering a possible increase on the frequency of inter particle collisions, favored by the shorter inter particle separation distances, should be considered. On the contrary, a true diameter length of 4,6 is obtained when the nanofluid is prepared with 10nm particles at 0.3% v/v. This nanofluid condition is the same as the one prepared by Choi et al. [66]. This true diameter length means that the surfaces between two

neighbor particles will be separated by 46 nm. We may expect that the larger inter particle separation distances would not favor the enhancement in thermal conductivity, at least on a collision frequency basis.

Evidently, there is a strong need to establish well defined and controlled procedures for thermal conductivity measurements in order to maximize their reliability and reproducibility.

5 CONCLUSIONS AND FUTURE WORK

We have successfully synthesized well-crystallized copper nanoparticles in both, aqueous media using hydrazine as reductant agent, and non-aqueous media using ethylene glycol. The nanoparticle size was tuned by a suitable control of the experimental conditions in both approaches. Proper selection of the synthesis conditions allowed us to achieve a fine control on the reducing conditions, the Cu forming reaction rate, and hence, on the average crystallite size of final solids. The rate at which Copper was strongly dependent on the excess of hydroxyl species in solution, heating intensity and initial concentration of starting Cu(II) species. The suitable selection of these parameters allowed a faster dissolution of the intermediate compounds (Cuprous oxide or alcoxide precursors in polyol medium) and subsequent reduction of the Cu(I) ions. Under optimum conditions, the average crystallite size of the Cu nanoparticles could be varied in the 10nm-20nm range. The use of surfactants (CTAB) and soluble polymers like PVP lead to a further decrease in crystallite size; nevertheless, the extremely high stability of those nanoparticles in the solvent made their removal a very difficult task.

The present thesis also addressed main limitations in the thermal conductivity measurement set-up based on the THW approach. The critical conditions, such as geometry and surface treatment of Pt wire, thermal isolation of the measuring cell from surroundings, were identified and the related problems overcome. As a result, a more reliable thermal measurement device, with an automatized data acquisition system, was developed.

Our results confirmed the enhancement of the thermal conductivity of the base fluid (ethylene glycol) when hosting Cu nanoparticles. The relative thermal conductivity of the base fluid was increased up to 32% when the nanofluid contained 7.5 v/v% of 20nm Cu nanoparticles.

Future work will be focused on the preparation of various nanofluids bearing metals as well as oxide nanoparticles. The nanoparticles will be synthesized in polyol or water under size-controlled conditions and effective options for their removal and re-suspension in base fluid developed. In order to study the effect of the size of nanoparticles, particularly for <10nm particles, on the nanofluid thermal and electrical conductivity, surfactant-coated crystals will be synthesized. Therefore, the influence of the surfactant on the thermal and electrical conductivity of the fluid will also be investigated.

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