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Thermomagnetic characterization of organic-based ferrofluids prepared with Ni ferrite nanoparticles

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ABSTRACT

In this work, a thermomagnetic characterization of kerosene-based ferrofluids (FFs) prepared with Ni-ferrite nanoparticles (NPs) is performed by measuring their thermal conductivity and diffusivity coefficient enhancements. The particles were synthesized by high-energy ball milling, as an alternative to the most commonly chosen NPs synthesis methods for FFs. The action of an applied magnetic field on the FF increases the thermal conductivity and diffusivity due to cooperation between the NPs, as it agglomerates them favoring chain-like and clusters formations. It was found that the heat capacity of the studied FFs decreases under the application of a magnetic field. The obtained results for thermal conductivity of FFs under magnetic fields were fitted by a gas-compression model that considers NPs agglomerates in the fluid.

1. Introduction

Ferrofluids (FFs) are considered advanced functional materials as they can be used to tailor the outcome in different devices by the action of an applied magnetic field. The specific properties of the FFs' free surfaces in presence of external magnetic fields are related to magnetoviscous and magnetorheologic effects [1]. In particular, during the last decade, the use of FFs as a heat-transfer medium has attracted much interest [2,3] because when the FFs are put under the influence of a magnetic field, not only their magnetic and rheological properties drastically change, but also their thermal properties. The involved processes are usually very fast [4] and, in general, reversible [5,6].

The possibility of inducing and controlling the heat transfer and the flux of fluid processes with a magnetic field, opened a window for a huge spectrum of promising applications, including devices such as thermo-siphons for technologic purposes, coolers of high power electric converters, and magnetically controlled heat-transfer devices in energy conversion systems [7].

The use of nanoparticles (NPs) for increasing the heat transfer of liquids offers several advantages [8] in comparison to the use of conventional fluids (non-magnetic nanofluids). One of them is the possibility of avoiding the implementation of complex devices with removable parts (commonly used for energy conversion and cooling devices) because a huge current of FF can be generated by temperature gradients and non-uniform magnetic fields. Therefore the thermophysical properties of FFs, such as thermal conductivity and viscosity can be modified by applying external magnetic fields [1–3,9].

Conventional liquids used for heat-transfer devices (water, oil, ethylene glycol, kerosene and others) can be a good choice for advanced applications if magnetic NPs are incorporated, but additional requirements are needed, such as high thermal conductivity and thermal expansion coefficient, low heat capacity, among others.

The thermal conductivity of different nanofluids-appropriate for heat transfer devices- has been investigated as a function of the carrier-liquid, the material of dispersed NPs, the NPs size distribution and the volumetric concentration of the FF, among other parameters. Several authors, such as Patel et al. [10], have measured the thermal conductivity (k) of nanofluids, finding that it is strongly modified by different parameters, such as concentration (volumetric fraction of NPs in the fluid) and those of the NPs dispersed in the fluid, such as size and composition. Besides, several studies (see, for instance the work of Phillip et al. [11]), have

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demonstrated important enhancements in the conductivities of nanofluids prepared with magnetic NPs after applying magnetic fields [12–15].

Magnetic NPs of metallic oxides such as Fe_3O_4, γ-Fe_2O_3 and Mn, Zn, Co or Ni ferrites are the most used ones in FFs due to their good chemical stability and high saturation magnetization. Magnetic NPs of metallic oxides are usually prepared by chemical methods such as sol-gel and co-precipitation, by microemulsions and phases reduction [3,16,17]. High-energy ball milling has also been successfully used to produce ferrite nanoparticles [18–23], and despite some controversy regarding the disadvantages of the method, it has proved to be a good alternative to the traditional chemical synthesis for many applications [19]. This technique allows obtaining significant amounts of the desired materials in relatively short milling times and it is effective for producing low-temperature solid-state reactions.

In our previous work [24], FFs prepared with Ni-ferrite ($NiFe_2O_4$) NPs synthesized by sol-gel were investigated, reaching enhancements in thermal conductivity of 50% under applied magnetic fields. We showed that if Gd ions are incorporated as doping element in the spinel structure, this modification increases the thermal conductivity of FFs up to 60% with an applied field of 400 Oe [24], due to the well-known magnetocaloric effect of Gd.

Although it is known that the most appropriate FFs for some biological applications are those prepared by chemical methods, mainly because of the narrow size distribution of the particles, this draw-back does not seem to be relevant for heat transfer applications. In this sense, the milling is an alternative low-cost technique for large-scale NPs production as up to 5 g of nanometric powder can be obtained in short time one-step procedures. The mechanical process favors the formation of smaller (nanostructured) particles due to the collisions of the balls with the material and grinding bowls, obtaining in most cases a wide size distribution with some tendency to NPs agglomeration.

In this work, an organic-based FF was prepared with Ni-ferrite NPs synthesized by high-energy ball milling, using kerosene as organic carrier. This fluid was chosen because of its relatively high flash point and autoignition temperature (between 37 and 65 °C and 220 °C, respectively) which makes its use less risky than other solvents. Another advantages for using kerosene as a carrier are its commercial availability, long scale and industrial production, its versatility, chemical stability and low cost.

The aim of this work is to study the thermal variables –thermal conductivity and diffusivity, and heat capacity– of the prepared FFs under applied magnetic fields for possible applications in heat-transfer devices.

2. Materials and methods

2.1. Synthesis of nanoparticles

Ni ferrite NPs were synthesized in a high-energy ball-mill using NiO and Fe_2O_3 oxides as precursors, in stoichiometric amounts according to the reaction: $Fe_2O_3 + NiO \rightarrow NiFe_2O_4$. The milling was performed at 700 r.p.m. in stainless steel bowls with 7 WC balls, a ball-to-powder mass ratio of 35, and milling time of 20 h. This milling time is of the same order as the time reported by other authors for the synthesis of similar systems [25,26]. The obtained powder was labeled M.

2.2. Preparation of ferrofluids

For preparing the FFs, the following substances were used: deionized milliQ water, sodium hydroxide (25% w/w), oleic acid, nitric acid (10% v/v), kerosene, acetone, and distilled water. 200 mg of Ni ferrite ($NiFe_2O_4$) were weighted (sample M) and were suspended in 20 mL of deionized water. Ten drops of sodium hydroxide solution were added up to pH 10 and the final solution was sonicated for 5 min. Stirring with a thin glass bar, 200 mg of oleic acid were added. Then, the system was heated at 95 °C while stirring and keeping the pH in 10. After cooling the solution, a diluted nitric acid solution (10% v/v) was added up to pH 6. For retaining the magnetic part of the solution, a magnet was located at the bottom of the container. The remaining was washed 4–5 times with water at 50 °C and twice with 1 mL of acetone for removing the water excess. Finally, the particles were dispersed in kerosene and sonicated during 3 h. Two FFs concentrations were prepared, 5 and 10% v/v which were labeled F-M5 and F-M10, respectively. Both samples remained stable for months.

2.3. Characterization techniques

X-ray diffractograms were measured in a Philips diffractometer using Cu Kα radiation. Spectra were collected in the 2θ range 20–70°, with a step-size of 0.02°, at a counting rate of 4 s per step. The morphology of samples was examined by Scanning Electronic Microscopy (SEM), and the images were analyzed with *ImageJ* software [27]. The magnetic properties of samples compacted in 1–2 mm thick disks were measured at room temperature (RT) in a vibrating sample magnetometer LakeShore 7200 with a maximum applied field of 1.5 T (15 kOe).

The transient hot-wire method [45] was used to determine the thermal conductivity and diffusivity of the prepared FFs. For this purpose, a home-made device was designed with dimensions and characteristics such that it can be used under a magnetic field of different intensities. The heat capacity of the FFs was also determined.

2.4. Thermal variables

The increment in conductivity can be calculated as $I = [(k_{FF} - k_0)/k_0]\cdot 100\%$ being k_{FF} and k_0 the FF and the kerosene thermal conductivities respectively, while the relative-to-kerosene diffusivity coefficient can be calculated as $\alpha_r = \alpha_{FF}/\alpha_0$ where α_{FF} and α_0 are the diffusivity coefficients of FF and kerosene, respectively.

For applications in heat-transfer devices, the results of thermomagnetic characterization can be properly represented by some parameters of particular interest, such as: thermal conductivity enhancement at zero field $I(H = 0)$, maximum enhancement of thermal conductivity I_{max}, magnetic field for which the maximum increment is produced, H_k; relative thermal diffusivity coefficient at zero field $\alpha_r(H = 0)$; the maximum diffusivity coefficient α_{rmax} and the field for which maximum diffusivity value is produced H_α.

The heat capacity of prepared FFs can be calculated using the expression $C_P = k/(\rho\cdot\alpha) = k/[(x\rho_{NP} + (1 - x)\rho_f)\cdot\alpha]$, where ρ, ρ_{NPs} and ρ_f are the FF, NPs and base fluid densities respectively, and x is the volume fraction of NPs for each magnetic field intensity. C_{Pr} is the relative-to-kerosene heat capacity, calculated as the ratio of the heat capacity of the FF to kerosene.

3. Results and discussion

3.1. NPs characterization

Fig. 1(a) shows the X-ray diffractogram of the obtained powder after the milling. The diffraction pattern was indexed using JCPDS cards N° 10-0325 for Ni-ferrite and N° 73-0603 for hematite. A small percentage of hematite Fe_2O_3 ($\leqslant$10%) is noticed, which indicates that the reaction was not complete. Usually, the presence of this kind of secondary phase can be eliminated either by further milling or an adequate thermal treatment [28,29]. However, in this