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Synthesis and characterization of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ and Fe_3O_4 nanoparticle ferrofluids for thermo-electric conversion

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Ferrofluids containing nanoparticles of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ (MZ5) and Fe_3O_4 (Magnetite) have been examined as potential thermal transport media and energy harvesting materials. The ferrofluids were synthesized by chemical co-precipitation and characterized by EDX to determine composition and by TEM to determine particle size and agglomeration. A range of particle coatings and carrier fluids were used to complete the fluid preparation. Commercially available ferrofluids were tested in custom built rigs to demonstrate both thermal pumping (for waste heat removal applications) and power induction (for power conversion and energy harvesting applications). The results indicate that simple ferrofluids possess the necessary properties to remove waste heat, either into thermal storage or for conversion to electrical power.

1. Introduction

A Ferrofluid is a colloidal suspension of ferromagnetic nanoparticles held within a carrier fluid [1]. The carrier can be a solvent, hydrocarbon oil or aqueous liquid dependent on use. Long chain surfactants, for example oleic acid, are used to coat the nanoparticles in order to inhibit flocculation [2]. As the nanoparticles are around 10nm in size they are subject to Brownian motion which keeps them suspended in the carrier fluid.Their uses include the role of a cooling medium in loudspeakers and high power transformers, inkjet printer fluid, hard drive motor bearings, mineral separation, and (since they have a high reflectivity) as an adjustable surface fluid mirror [3-7]. The combination of suspended magnetic particles and carrier fluid give the resulting colloid the ability to change fluidic properties, most notably viscosity, in the presence of an external magnetic field. The carrier fluid, a dominant part of the system, has a great impact on physical properties such as viscosity and evaporation [8]. Since the ferromagnetic particles are of nanometer dimension, the long range ordering produces only single domains and fixed dipole magnetic fields [9]. The suspended nanoparticles in a ferrofluid, having magnetic single-domains, possess a magnetic moment, µ. When subjected to an applied external magnetic field, B the magnetic moments have a potential energy, U, given by Equ. 1. In order to reduce U the nanoparticles orient parallel to the applied magnetic field lines. When removed from the field the magnetic moments rapidly become randomised and magnetisation becomes zero [10].

$$U = -\mu B \qquad \text{Equ.1}$$

If the applied magnetic field has a gradient then the nanoparticles will experience a force, F, and move towards the region of greatest field intensity. This force is proportional to the applied magnetic field, B, and the magnetic moment of the nanoparticle, µ, Equation. 2

$$\mathbf{F} = \nabla \mathrm{B}\mu \qquad \text{Equ.2}$$

Another important parameter that affects the magnetic properties of ferrofluids is the Curie Temperature, T_c. Above T_c the atomic order within the magnetic domain is disrupted by thermal vibrations, the thermal energy overcomes the electronic exchange forces, reducing the saturation magnetization of the nanoparticles to zero as the disorder within the domains increases.

Heat transfer and pumping in ferrofluids has been extensively reported for both free convection and forced convection conditions. In the case of thermomagnetic free convection, experimental investigations with a varying magnetic field were published by Kikura et al [11] and Sawada et al [12], although the orientation of the magnetic field is unclear. Theoretical studies (analytical and numerical) of thermomagnetic free convection often suffer from shortcomings in the modeling of the magnetic field. For example, Finlayson[13], Lange [14] and Krakov and Nikiforov [15] all assumed a spatially uniform magnetic field, which is rarely the case with commercial dipoles. Similarly imprecise assumptions on the magnetic vector limit the applicability of the outputs from the theoretical work of Yamaguchi et al [16] and Tangthieng et al [17]. More fundamental issues are evident in the theoretical simulations of thermomagnetic forced convection, most notably in the analysis of Aihara et al [18] and Yamaguchi et al [19]; where the magnetic fields are in conflict with Maxwell's equations. This was corrected by Ganguly et al [20] who showed that the addition of line-source dipoles enhances heat flow, to a degree dependent on dipole strength and the geometry of the magnet (or the positioning of an electromagnet). Lajvardi et al [21] designed an experiment to study the forced thermomagnetic convection and heat transfer performance of magnetite (Fe_3O_4) nanoparticles in distilled water, attributing the measured increase in the local heat transfer coefficient in the presence of a magnetic field to either an increased thermal conductivity or specific heat capacity. Self-powered thermomagnetic convection loops (self-regulated pumping) using Mn-Zn based ferrofluids have been reported by Xuan and Lian [22], but did not include any measurement of the pump pressure achieved, except to state that it must exceed the viscous drag. Ferrofluid pumping in both time-varying and spatially-travelling magnetic fields has been modeled numerically by Zahn and Greer [23] and Mao and Koser [24], with the latter calculating ferrofluid flow velocities of the order of 5-10 mm/sec. Some values of pressure differences in experimental ferrofluid pumps have also been published, together with limiting effects. Later work by Mao and Koser [25] reports 1300 Pa in 2 x 0.25 mm microchannels. This compares with 177 Pa in 1 x 0.4 mm microchannels from

Xuan and Lian [26], when the fluid was deteriorating owing to bubble formation. Short term operation (limited by thermal instabilities) produced a maximum pressure of 345 Pa in 2 mm diameter glass tubing in the magnetite ferrofluid investigated by Pal et al [27].

In this work we describe the synthesis of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ (MZ5) and Fe_3O_4 (Magnetite) nanoparticles by chemical co-precipitation, their subsequent coating with oleic acid, and their suspension in ethylene glycol and heptane respectively.
Various material properties of comparable commercial ferrofluids are derived, before the suitability of the fluids for energy harvesting applications are investigated.

2. Materials and methods

To synthesis the magnetite nanoparticles the following process was followed; two 0.5 M aqueous solutions one of ferric chloride hexahydrate (98%, Aldrich) and the other ferrous chloride tetrahydrate (99%, Aldrich) where prepared and mixed together at room temperature. The resulting solution was added rapidly to a 4M NH_4OH (30%, Sigma-Aldrich) solution heated to 80°C under constant stirring using a non-magnetic agitator. The resulting black precipitate mixture was left to stir for 1 hour at 80°C ± 10°C.

To synthesis the MZ5 nanoparticles, 0.1M aqueous solutions of Manganese Chloride (98%, Aldrich), Zinc sulphate heptahydrate (99%, Aldrich) and a 2M solution of ferrous chloride tetrahydrate (99%, Aldrich) were prepared and mixed together at room temperature. The mixture was added rapidly to a 3M solution of NaOH (97%, Aldrich) under constant stirring with a non-magnetic agitator. The resulting mixture was left to stir for 1 hour at 80˚C.

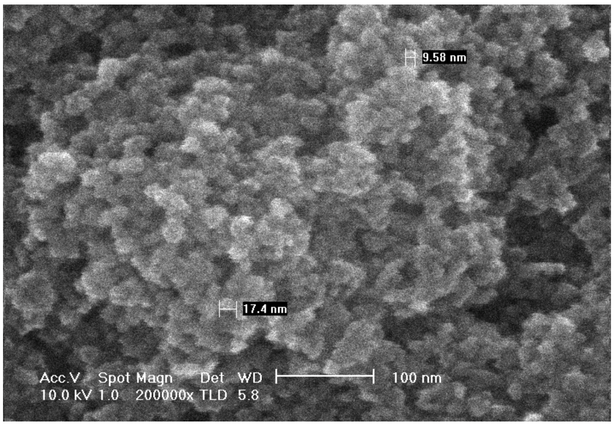

FIG 1. TEM of coated magnetite nanoparticles

Figure 1 shows a micrograph of oleic acid coated magnetite particles, with typical size in the 10-18 nm range.
The capping agent for both solutions was prepared by mixing oleic acid (90%, Sigma Aldrich) with NH_4OH in a 1:10 ratio by volume. A small quantity of this mixture was added to the magnetite and MZ5 mixtures and left to stir for a further 30 minutes at 80°C.

The resulting precipitates were separated from solution by placing a magnet below the reaction vessel and pouring out the waste fluid. The magnet was then removed and the precipitate washed with deionised water, the waste being removed as above the process being repeated multiple times. The final products were then dispersed in hydrazine for the magnetite particles and ethylene glycol for the MZ5 particles. Figure 2 is an EDX plot of composition for coated magnetite nanoparticles.

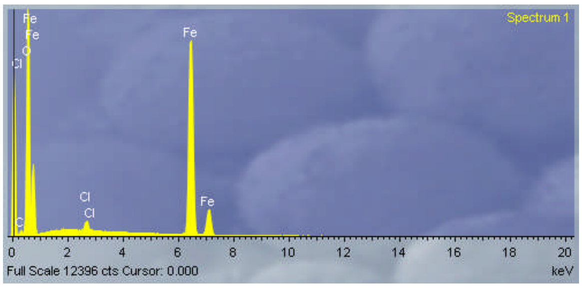

FIG 2. EDX analysis of coated magnetite nanoparticles

The concentration and type of the suspended nanoparticles, the surfactant, and the carrier fluid combine to impart the overall magnetic and rheological properties of the ferrofluid, most notably the magnetization and base viscosity. This offers the opportunity to tailor the ferrofluid to act in a closed system to provide the removal of thermal energy and its transport into a thermo-electric converter. This can be achieved in a two-stage process, as described below.

The first stage comprises a thermal pump, shown conceptually in Figure 3.

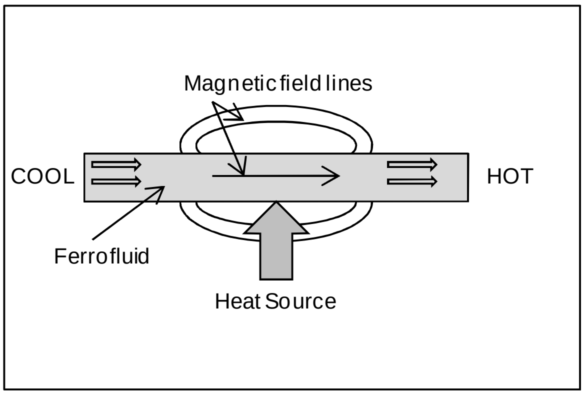

FIG 3. Ferrofluid as a waste heat collector, creating a pressure differential in the presence of an external magnetic field.

Ferrofluid is drawn into the heat affected zone where its temperature is raised, whereupon the magnetic properties of the fluid diminish. The creation of the demagnetized fluid, coupled with the cooler highly magnetized fluid behind the hot zone, creates a pressure differential given by [28]

$$\Delta P = \mu_0 H[M(T_{out}) - M(T_{in})] \qquad \text{Equ 3}$$

where μ_0 is the free space permeability, H is the externally applied magnetic field intensity, and M(T) is the temperature dependent magnetization of the nanoparticles within the ferrofluid. The pressure differential increases as the Curie temperature is approached, and the thermal pumping in a closed system relies on the removal of heat from the hot zone.

Thermal energy removal leads to the second stage in the thermo-electric conversion process, namely the conversion of the magnetic fluid motion into electrical output. Downstream from the thermal pump the moving magnetic field produces an induced emf in a suitably arranged Faraday coil, providing current through an appropriate load.

The cumulative flux on any coil is the sum of the flux produced by each of the magnetic fields emanating from the ferrofluid particles in suspension. Thus the individual magnetic particles need to be spun and magnetically aligned in order to maximize the rate of change of flux, for example by the introduction of controlled turbulence. Since the magnetic nanoparticles are single domain species they exhibit polar phenomenon and can be expected to align at any one point under the influence of an externally applied field. Figure 4 illustrates this dynamic induction stage of the TE converter.

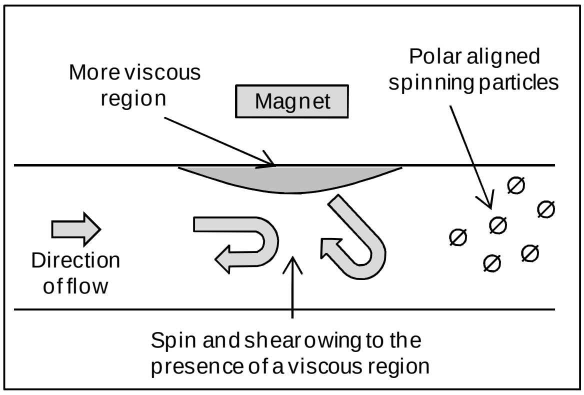

FIG 4. Influence of external magnetic field on magnetic nanoparticles

Maximizing the induced emf by the introduction of controlled turbulence suggested modeling of the ferrofluid using CFD [29]. To date, the ferrofluid has been modeled as a Newtonian fluid, with a linear stress to strain ratio, using Ansys v11 plus Flotran. These models analyzed the flows in a variety of pipe geometries and constrictions, prior to the construction of test rigs. Each pipe length was 20cm, with a 1cm^2 inlet diameter. The inlet diameter was set following early experiments with both 3.2mm and 9.5mm inner diameter Silastic tubing, where hardening of the fluid was observed in the smaller diameter tubing (although this could be attributed to a reaction between the isoparaffin carrier fluid and the tubing used in this trial). The ferrofluid was assumed to have a density of 1.5g/cm^3 with the same bulk modulus as water. Four pipe geometries were tested with fluids of 50 and 100cP viscosity and inlet flows of 1, 5, and 10cm/s. Figure 5 shows a vector plot output of an Ansys CFD for a 50cP fluid with input velocity 1 cm/s in a pipe with constrictions that are half of the bulk pipe diameter. The flow is essentially laminar, with an increase in speed of approximately five times at the constriction.

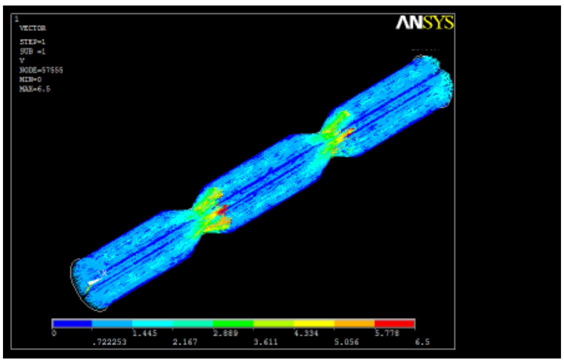

FIG 5. Vector Plot of Ansys CFD, 50cP, 1cm/s (constricted pipe)

3. Results and Discussion

To test the performance of the ferrofluids in the context of heat transport and energy harvesting a number of test rigs were designed and built. To demonstrate induced emf, LLDPE (Linear Low Density Polyethylene) 10 mm diameter hydraulic tubing and Neodymium rectangular magnets (25x10x5mm) were used in a closed loop with a Totton DC 15/5 centrifugal pump and a tightly wound copper wire coil, in an arrangement shown in Figure 6 below.

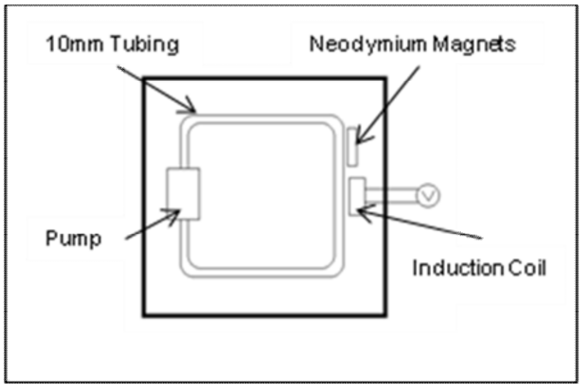

FIG 6. Ferrofluid - Induced emf test rig

Three separate commercial ferrofluids were tested in the induced emf test rig. These were all of Fe_3O_4 (magnetite) composition, with differing viscosities and saturation magnetization. The results are shown in Figure 7 for an exit speed of 6cm/s for the three Fe_3O_4 based fluids, in both laminar flow and turbulent (manually pulsed) flow. The three samples consisted of (i) 200G/200cP magnetite with approximately 10nm nanoparticles in synthetic oil, (ii) 600G/30cP magnetite with approximately 10nm particle size in isoparaffin, and (iii) a 50% mix by bulk volume of the fluids described in (i) and (ii).

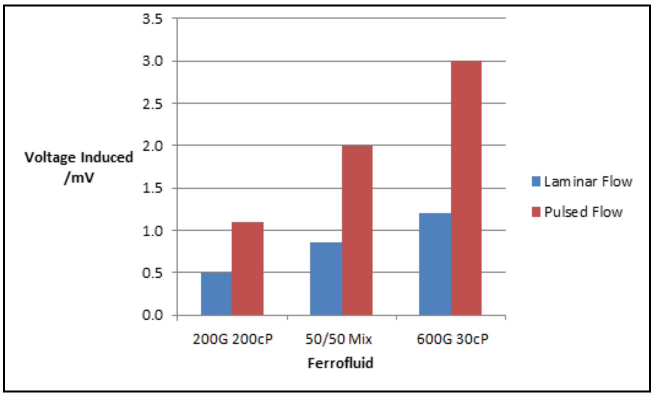

FIG 7. Induced emf voltage : Fe_3O_4 based ferrofluids

The induced emfs (up to 3.0 mV in these "proof of concept" trials) demonstrate the potential for energy harvesting, provided that the conditions for closed loop thermal pumping can be established.

The rig designed to demonstrate the action of a ferrofluid as a thermal pump is shown in Figure 8, and consists of a closed glass tube with a 15° incline. A permanent magnet and a wound rope heater were positioned as shown. A magnetite ferrofluid (320G/200cP) was used in the trial, and operated at 120°C. When operated the fluid was shown to travel 5cm along the inclined tube establishing a head of pressure equivalent to 190 Pa. This compares to the pressure calculated using Equ. 3 of 208 Pa, including an estimation of the magnetic field intensity in the ferrofluid from the known field at the face of the magnet.

Considering the energy required to establish the head of pressure and the thermal energy required to heat that head of fluid to the operating temperature a thermomechanical conversion efficiency (mechanical movement realized/input thermal energy) of 0.13m% can be calculated. In comparison the theoretical maximum efficiency of a heat engine derived by the Carnot cycle is 13.4%. A further increase in efficiency could be obtained if the temperature induced change in magnetization were increased to a greater degree than the thermal energy required to bring about the temperature change. For magnetite this is unlikely to occur until the ferrofluid is heated in excess of 200°C as it is not until the Curie temperature is approached that changes in the magnetization outweigh the additional thermal burden. It should be noted that even here, the efficiency is only likely to increase by a few factors, and not orders of magnitude. For much larger increases in efficiency the externally applied magnetic field needs to be increased (equation 3). Given the apparent difference in actual and theoretical pressures, one way of increasing the efficiency would be to reduce the size of the fluidic structure such that the magnets could be placed closer to the ferrofluid. Based on the observations above an order of magnitude increase in magnetic field could be potentially achieved with the existing magnet system and smaller fluidic channels positioned closer to the magnet, thereby increasing the efficiency. Further increases in efficiency would require the external magnetic field to be increased.

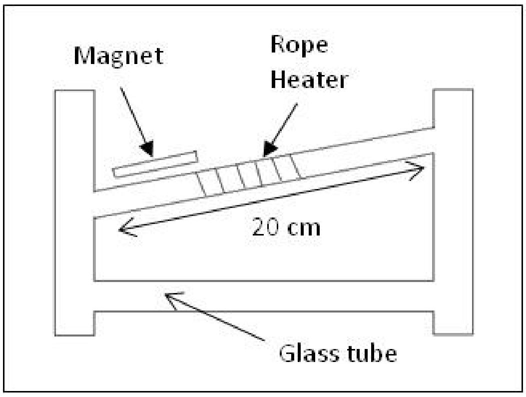

FIG 8. Ferrofluid – thermal pump test rig

4. Conclusions

Ferrofluids containing nanoparticles of Fe_3O_4 (magnetite) and $Mn_{0.5}Zn_{0.5}Fe_2O_4$ (MZ5) have been synthesized and characterized. Samples of commercially available ferrofluids were examined as to their potential as thermal transport media. The ability of a ferrofluid to act as a thermal pump has been demonstrated, and we have calculated a thermomechanical conversion efficiency (mechanical movement realized/input thermal energy) of 0.13m%. In an inclined tube a pressure differential of 190 Pa can be inferred, compared to a calculated pressure (Equ. 3) of 208 Pa. Furthermore a ferrofluid, once sufficient flow has been established, has been shown to induce a usable emf in a coil proximal to the fluid flow. In summary then, ferrofluids of the appropriate Curie temperature and fluid properties, together with reasonable turbulence, can find applications in cooling, heat transfer, and energy harvesting.

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