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Nanotechnology Enabled Advanced Industrial Heat Transfer Fluids

FINAL REPORT

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INTRODUCTION

Many industrial sectors (e.g., agricultural, pharmaceutical, materials manufacturing, and oil refineries), transportation, solar energy and electronics, use heat transfer fluids for heating, cooling and recovering waste heat. Improving the thermal properties of fluids for transferring heat more efficiently will save energy. Utilizing heat transfer fluids with high thermal conductivity will help reduce the overall manufacturing cost, and simultaneously help protect our environment by reducing emission of green house gases. A thermal fluid is analogous to steam in a process heating system for transferring high temperature energy in closed-loop low-pressure systems in chemical and manufacturing industries. In case of transportation applications, an improved heat transfer fluid will lead to improvement in the performance of the engine, by allowing it to operate at a higher temperature, which is needed to reduce the fuel consumption and the emission of carbon monoxide and unburned hydrocarbons[1]. The goal of this program was to develop nanoparticle containing heat transfer fluids (e.g., antifreeze, water, silicone and hydrocarbon-based oils) that are used in transportation and in the chemical industry for heating, cooling and recovering waste heat. These **Nanofluids**, as they are called, have significantly higher thermal conductivity than the base fluid, thereby having improved heat transfer properties.

Nanofluids can increase the thermal conductivity of heat transfer fluids because of the large surface area of nanoparticles as heat transfer takes place on the surface of particles. Previously, it has been shown that adding nanoparticles in a fluid can significantly enhance the thermal conductivity of the base fluid[2]. However, a majority of the research work performed to date do not apply directly to real-life applications. For example, Eastman et al[3] demonstrated that adding 0.3 vol% Cu nanoparticles in pure ethylene glycol can enhance the thermal conductivity more than 40%. However, engine coolants although based on ethylene glycol, have a large number of additives that change the interaction between the fluid and the particles. Choi et al.[4] demonstrated that adding carbon nanotubes (~ 1 vol%) into Poly(?-olefin) fluid enhances the thermal conductivity of the fluid by ~160%. On the other hand, Xie et al.[5] observed that increase in conductivity was only ~ 20% on adding 1 vol% carbon nanotube in a non-polar liquids such as decene. The precise reasons for this discrepancy are not known, and it was postulated that differences in preparation methods and carbon nanotube specifications might have been responsible for this difference. Moreover, the high cost of the carbon nanotubes and issues with practical long term use makes them difficult to be utilized in the cost conscious transportation and industrial sectors. Our own work in a previous program[6] showed that dispersing a small amount of nanoparticles of Al_2O_3 in a **commercial coolant** can improve the thermal conductivity of the fluid in the range of 10 – 14% (see section 1.c.4). But for most applications, our industrial partners have communicated to us that for a good value proposition warranting the use of Nanofluids demands that the thermal conductivity be increased by at least 30% (*provided other fluid characteristics are unaltered*). **The Phase I program has overcome this shortcoming by demonstrating that the addition of economically manufactured magnetic Fe_3O_4 nanoparticles in commercial fluids leads to exceptional increases in thermal conductivity.**

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[1] H.H. Pang and C.J. Brace, Proc. Instn. Mech. Engrs. vol 218 Part D: J. Automobile Engineering, page 1209 (2004).
[2] J. A. Eastman, S. R. Phillpot, S. U. S. Choi, and P. Keblinski, Annu. Rev. Mater. Res., **34**, 219 (2004).
[3] Dr. Jeff Eastman is a collaborator of NEI in this program, and was an STTR partner of a previous program on fluids; Eastman et al., Applied Physics Letters, **78**, 718 (2001),
[4] S.U.S. Choi, Z.G. Zhang, W. Yu, F.E. Lockwood, and E.A. Grukle, App. Phys. Lett., **79** (14), p 2252 Oct. 2001
[5] Xie et al., Journal of Applied Physics, **94**, 4967 (2003).
[6] Phase II STTR program (between NEI and Argonne National Laboratory); Grant No: DE-FG02-01ER86136

Previously, Eastman and coworkers[2] had postulated that clustering of nanoparticles in the fluid can facilitate a low thermal resistance path for phonons, thereby imparting a substantial enhancement in the thermal conductivity. However, it is impractical to achieve such nanoparticle clustering in a fluid via a percolating network, since it would lead to agglomeration of the nanoparticles and an unacceptable increase in viscosity. Our Phase I results, described below, suggest that it is possible to create **"transient" nanoparticle clustering** by applying an external magnetic field on fluids containing magnetic nanoparticles. Application of a magnetic field on magnetic nanofluids not only led to a significant increase in the thermal conductivity, but also preserved the stability of the nanofluids.

The successful Phase I program has laid the foundation for implementing Nanofluids in a number of heat transfer fluid applications. A provisional patent application has already been filed for the invention (Serial No. 60/765,682), details of which are presented in the section on Commercialization. The following were the major Phase I accomplishments, leading us into the next phase of product development:

(1) Demonstrated for the first time (*to the best of our knowledge*)[7] more than 150% increase in thermal conductivity of a Nanofluid upon the application of a magnetic field, Error! Reference source not found..
(2) Formulated stable magnetic nanoparticle dispersions in water and several **commercial** heat transfer fluids such as antifreeze, Paratherm NF and PAO. PAO was provided to us by Chevron Philips, while the antifreeze was supplied by Recochem Corporation, who is one of our industrial partners in the proposed Phase II program.
(3) Demonstrated that the thermal conductivity of water-based suspensions can be increased to 40% by adding only ~ 3vol% Fe_3O_4 nanoparticles, Error! Reference source not found..
(4) Measured the thermal conductivity of a variety of nanofluids, and observed that increase in the conductivity of magnetic nanofluids in presence of a magnetic field is correlated with the viscosity and the aggregate size of nanoparticles in the dispersion, indicating that thermal conductivity of fluids can be further enhanced by optimizing the surface chemistry of nanoparticles.
(5) Established several product development partnerships:

a. **Ford Motor Company**: Researchers at Ford have tested our Nanofluid samples, and are enthusiastic with the new results on improved thermal conductivity;
b. **Deere & Co.**: Engineers at Deere & Co. have a deep interest in utilizing Nanofluids to increase the power density of their off-road vehicle systems;
c. **Recochem Corporation**: Recochem is the exclusive supplier of engine coolants to Deere & Co., and has a vested interest in supplying improved engine coolants. Recochem has performed a number of ASTM standard tests on our Nanofluids;
d. **Red Bull Racing**: The UK-based 'Formula One Team' company is attracted by the possibility of utilizing Nanofluids to improve the efficiency of the cooling system, and has embarked on a Nanofluids testing program;
e. **Duratherm**: The provider of thermal fluids (both polar and non-polar) intends to utilize NEI's Nanofluid technology to be able to supply a new class of fluids;

Following is a synopsis of the experimental work that was performed during the course of the Phase I program

[7] There are some theoretical studies on augmenting heat transfer in magnetic fluids (by R. Ganguly, S. Sen and I. K. Puri, J. Magnetism and Magnetic Materials, vol. 271, 63 (2004)), but no practical consideration to improving the thermal conductivity has been given

A. Objectives

The primary objective of the Phase I program was to demonstrate that a significant increase in the thermal conductivity of a heat transfer fluid can be achieved by incorporating magnetic nanoparticles in the fluid. The other objectives were:

(i) to evaluate the effect of nanoparticle additives on the flow characteristics of the base fluid, and

(ii) to determine important parameters (e.g., aggregate size and surface characteristics of nanoparticles) that make a significant impact on the thermal conductivity of the base fluid. Since the chemistries of individual heat transfer fluids are significantly different from each other, nanofluid properties (e.g., stability and viscosity) will also vary, which will eventually affect the overall thermal properties.

We have successfully accomplished all of the above mentioned objectives.

In Phase I, emphasis was placed on dispersing Fe_3O_4 nanoparticles in both polar (e.g., water, antifreeze) and non-polar (e.g., hydrocarbon and silicone –based oils, and poly(? - olefin)) heat transfer fluids. Thermal conductivity of nanofluids, with and without a magnetic field, was measured by a Decagon KD2 Thermal Properties Analyzer based on the single needle heat pulse technique. Measurements were made under both a constant and a varying magnetic field.

To the best of our knowledge, this is the first time that anybody has shown that the thermal conductivity of a magnetic fluid can be substantially enhanced upon application of an external magnetic field. What follows is a synopsis of the experimental work that was performed during the course of the Phase I program.

B. Synthesis of Nanofluids

This section describes the synthesis of magnetic nanoparticles, suitable surface modification, and dispersion in an array of heat transfer fluids.

B.1 Synthesis of Fe_3O_4 nanoparticles

Fe_3O_4 nanoparticles were synthesized using a proprietary method developed by NEI. In this process, a dilute solution of ammonium hydroxide was prepared in a reactor using deoxygenated water. A proprietary surface modifier was then added to the reactor. In a separate container, an iron salt solution was prepared by dissolving salts containing Fe^{2+} and Fe^{3+} species, combined stoichiometrically in deoxygenated water. This container is covered and a nitrogen purge was used to prevent the introduction of oxygen. A bubbling nitrogen purge was then established through the reactor flask, followed by addition of the iron salt solution using a precalibrated peristaltic pump while stirring vigorously. Rapid precipitation of Fe_3O_4 resulted, and upon completion of the salt solution addition, Fe_3O_4 nanoparticles settled to the bottom of the reactor. The supernatant liquid was then pumped off and the Fe_3O_4 slurry was extracted and washed using a centrifuge. All remaining water was removed at low temperature under vacuum.

Powder X-ray diffraction data (**Figure 1**) shows that the as synthesized powder is pure phase Fe_3O_4. Surface area of this powder is ~ 128 m^2/g, which is almost three times higher that that of commercially available nanopowders. For comparison purposes, nano – Fe_3O_4 powder was also obtained from Aldrich Chemicals; the surface area of this powder was only ~ 40 m^2/g.

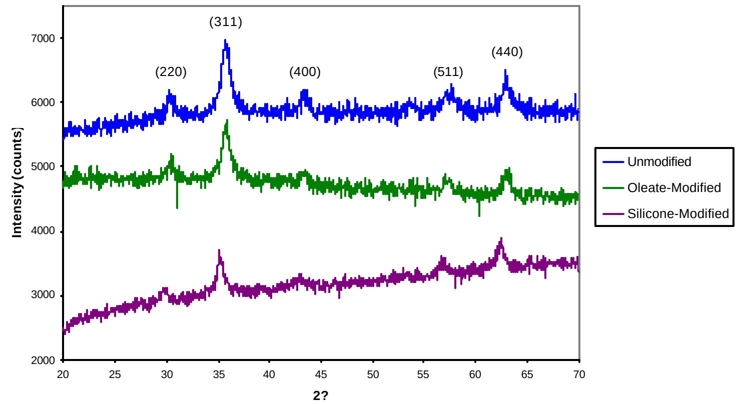

Figure 1: X-ray diffraction data of unmodified and modified Fe_3O_4 nanopowders that were synthesized during the course of the Phase I program.

B.2 Synthesis of surface modified Fe_3O_4 nanoparticles

(i) Oleate-modified Fe_3O_4 Nanoparticles

Previously[8], it has been shown that hydrophobic Fe_3O_4 nanoparticles can be produced by modifying the surface of nanoparticles with oleate ions. A similar process was utilized to produce oleate coated Fe_3O_4 nanoparticles. Such hydrophobic nanoparticles can be dispersed in non-polar fluids, such as hydrocarbon oils.

The procedure used was similar to NEI's proprietary method, described above for aqueous synthesis, except the initial addition of surface modifiers was omitted. Instead, oleic acid was added upon completion of the precipitation reaction. Oleate-modified nanoparticles then began to settle because of their hydrophobic nature. Once the precipitate had settled, the supernatant liquid was pumped off and the remaining slurry was centrifuged, washed twice with distilled water and a third time with a mixture containing equal volumes of distilled water and acetone. The final cake was dried under vacuum for 8 hours at 60°C, resulting in a thick black paste which was then stored under nitrogen. TGA (**Figure 2**) was performed on the final paste to determine the degree of surfactant adsorption. The surfactant was found to make up approximately 37% of the final paste. The powder was pure phase Fe_3O_4 (Figure 1).

[8] M.T. Lopez-Lopez, J. D. G. Duran, A. V. Delgado and F. Gonzalez-Caballero, *Journal of Colloid and Interface Science*, **291**, 144 (2005).

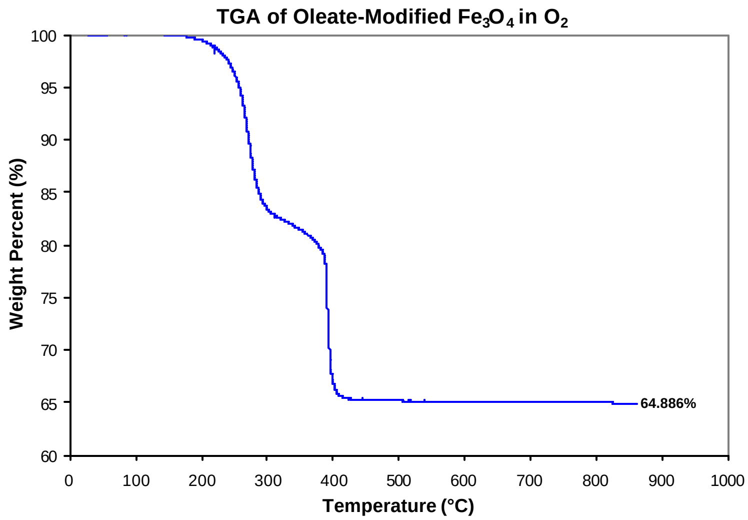

Figure 2: Thermogravimetric Analyzer data of oleate-modified Fe_3O_4 nanoparticles in an oxygen atmosphere.

(ii) Silicone-modified Fe_3O_4 Nanoparticles

In addition to synthesizing oleate-modified nanoparticles, an attempt was also made to produce nanoparticles modified with a silicone group, so that the nanoparticles will be compatible with silicone oil-based heat transfer fluids. Silicone modified Fe_3O_4 nanoparticles were produced using a silicone-based surfactant, predispersed in water by stirring followed by ultrasonication in a warm water bath for 15 minutes. The surfactant addition is analogous to that described above for oleate modification. TGA (**Figure 3**) was performed on the final powder and on the silicone surfactant to estimate the degree of surfactant adsorption. Surfactant was estimated to make up approximately 20% of the final powder.

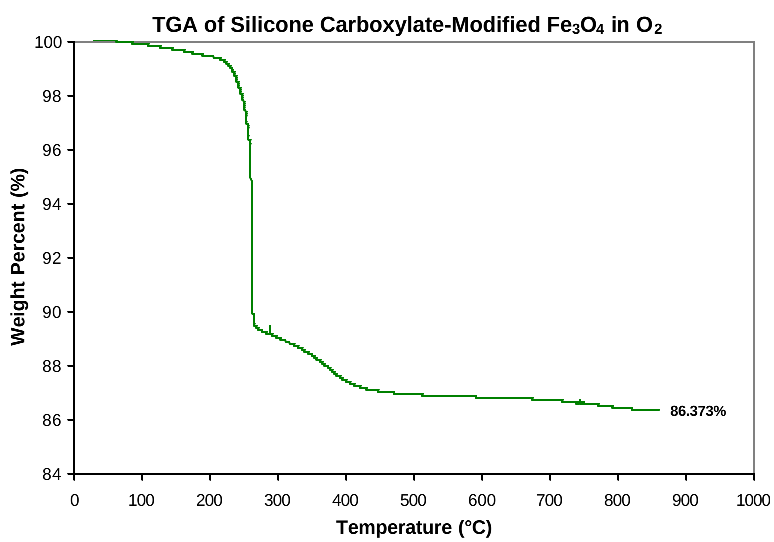

Figure 3: TGA of a silicone-modified Fe_3O_4 nanoparticles in an oxidizing atmosphere.

B.3 Dispersions of Fe_3O_4 nanoparticles in polar and non-polar fluids

(i) Polar Fluids

Unmodified Fe_3O_4 nanoparticles that were produced using the solution method described above were dispersed in both pure water and engine coolant/water solutions. For comparison purposes, in a few instances, commercially available Fe_3O_4 nanoparticles were also utilized. The surface of the nanoparticles in solution was modified by adding tetramethylammonium hydroxide (TMAH) in solution. $N(CH_3)_4^+$ groups of TMAH adsorbs on negatively charged Fe_3O_4 nanoparticles, and stabilizes nanoparticles by joint contributions of electrostatic forces of charged particles and steric hindrance. The surface modification of Fe_3O_4 nanoparticles with TMAH is depicted in **Figure 4**.

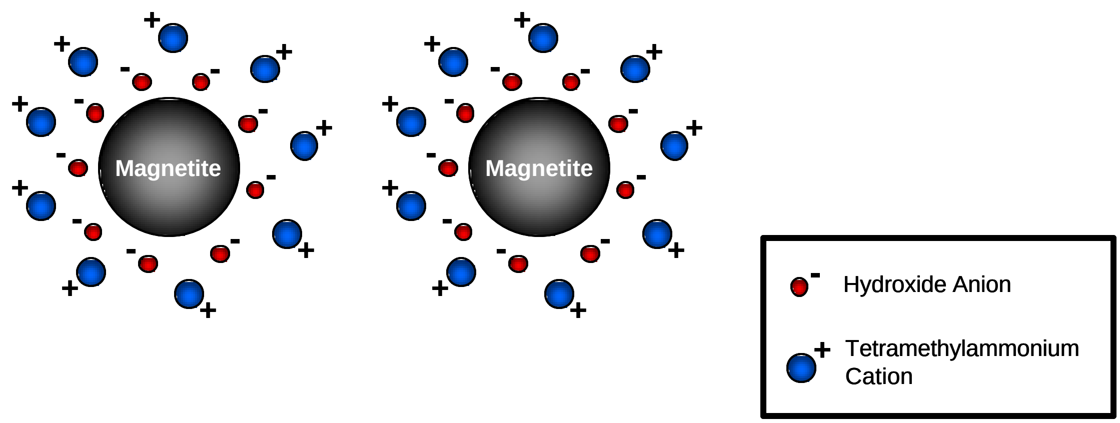

Figure 4: A schematic illustrating the surface modification of Fe_3O_4 (Magnetite) nanoparticles with TMAH in polar solutions. This figure is adopted from the reference[9].

Water-based Suspensions**:** In 125mL Erlenmeyer flasks, distilled water was prepared with various concentrations of tetramethylammonium hydroxide (25% w/w aqueous, Alfa). Fe_3O_4 nanoparticles were then added to these solutions for loadings of 5, 10 and 15 wt% nanoparticles. Ultrasonication was then used to disperse the particles.

Engine Coolant (OAT)-based Suspensions: In 250mL beakers, distilled water was prepared with various concentrations of TMAH, followed by the addition of a glycol-based engine coolant (OAT coolant, supplied by Recochem Inc.), maintaining an equal volume ratio of water and glycol. This mixture was briefly stirred prior to adding Fe_3O_4 nanoparticles for sample loadings of 5, 10 and 15wt%. The particles were then suspended thorough the use of a high shear mixing system followed by sonication in sealed flasks.

(ii) Non-polar Fluids

Initially, attempts were made to disperse unmodified Fe_3O_4 nanoparticles in commercial heat transfer non-polar fluids with the aid of oleic acid. However, in majority of cases, the suspensions were unstable, and phase separated upon application of an external magnetic field. In light of these results, we decided to synthesize suspensions using surface-modified Fe_3O_4 nanoparticles.

Hydrocarbon-based Heat Transfer Fluids – PAO 4cSt (Chevron Phillips, LLC), and Paratherm NF (Paratherm Corp.): In 250mL beakers, the nonpolar fluid was combined with oleate-modified Fe_3O_4 nanoparticles for sample loadings of 5, 10 and 15 wt%. The particles were

[9] Voh.chem.ucla.edu/classes/magnetic_fluids/pdf/ferrofluid%20Teacher%20Manual2

then suspended thorough the use of a high shear mixing system. Finally, mixed samples were transferred to sealed flasks and sonicated.

Silicone-based Heat Transfer Fluid - Syltherm S800 (Dow Chemical): In 250mL beakers, Syltherm was combined with silicone-modified Fe_3O_4 nanoparticles for sample loadings of 5, 10 and 15 wt%. The particles were then suspended thorough the use of a high shear mixing system. Finally, mixed samples were transferred to sealed flasks and sonicated.

C. Nanofluid Viscosity and Aggregate Size of Nanoparticles

Viscosity testing was performed for all samples at room temperature using a Brookfield DV-II+PRO Viscometer. Viscosity was recorded as a function of shear rate for each particular fluid. **Aggregate particle size** for each sample was also measured with light scattering in a Coulter N4 particle size analyzer. Results with a brief discussion for each group of samples are presented below.

C.1 Non-Polar Nanofluids

Paratherm NF[10]-based suspensions demonstrated good dispersion quality with an aggregate particle size of ~ 250nm. Suspension stability was fair for all samples, with increased settling at higher loadings after extended static periods. The settled particles could be returned to the suspension with gentle agitation. Rheological behavior (**Figure 5**) of these fluids demonstrated nearly Newtonian flow characteristics at 5wt%, but became increasingly non-Newtonian at 10 and 15wt%.

Paratherm NF-based Suspensions at 20°C

Sample ID	Loading	Aggregate Size (nm)	Viscosity @40s^{-1} (cP)
PT-B	0%	-	39.2
PT-5A	5%	258.5	46.4
PT-10A	10%	236.5	65.2
PT-15A	15%	257.9	92.2

[10] Paratherm NF was provided to us by the Paratherm Corporation. We wanted to pursue the interaction but our contact at Paratherm left the company. We tried to connect with his replacement, but were unable to do so. We then turned to Duratherm, who is eagerly supporting the Phase II program.

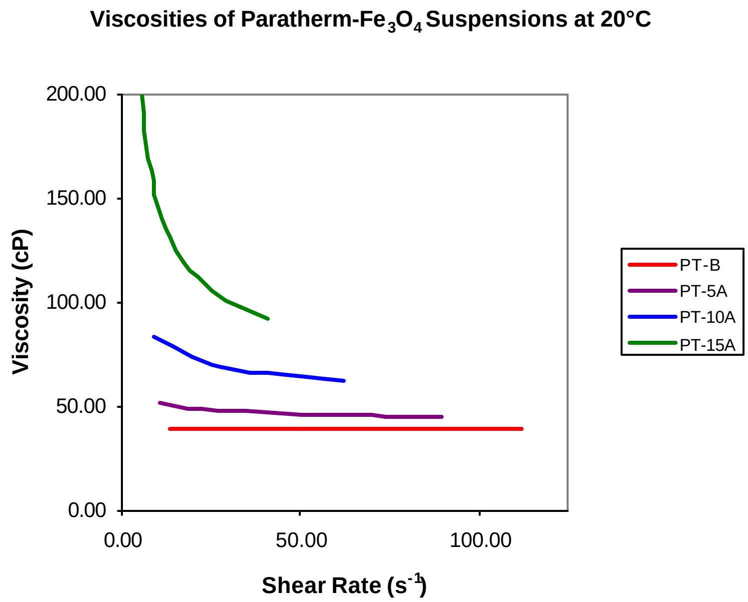

Figure 5: Rheological behavior of Paratherm NF- Fe_3O_4 suspensions at 20 °C, indicating that nanofluid containing 5 wt% Fe_3O_4 nanoparticles exhibited nearly Newtonian flow.

Syltherm S800-based suspensions demonstrated fair to poor dispersion quality with aggregate sizes of ~ 450nm. Suspension stability was poor for all samples, with increased settling at higher loadings, as well as phase separation for all samples after extended static periods. Short term stability was good, lasting about 48 hours, and settled particles could be easily redispersed with agitation. Rheological behavior (**Figure 6**) of these fluids demonstrated slightly non-Newtonian flow characteristics at 5wt%, with substantially increasing non-Newtonian behavior at 10 and 15wt%.

Syltherm S800-based Suspensions at 20°C

Sample ID	Loading	Aggregate Size (nm)	Viscosity @110s^{-1} (cP)
S800-B	0%	-	10.2
S800-5A	5%	422.6	14.2
S800-10A	10%	468.9	24.0
S800-15A	15%	438.4	33.5

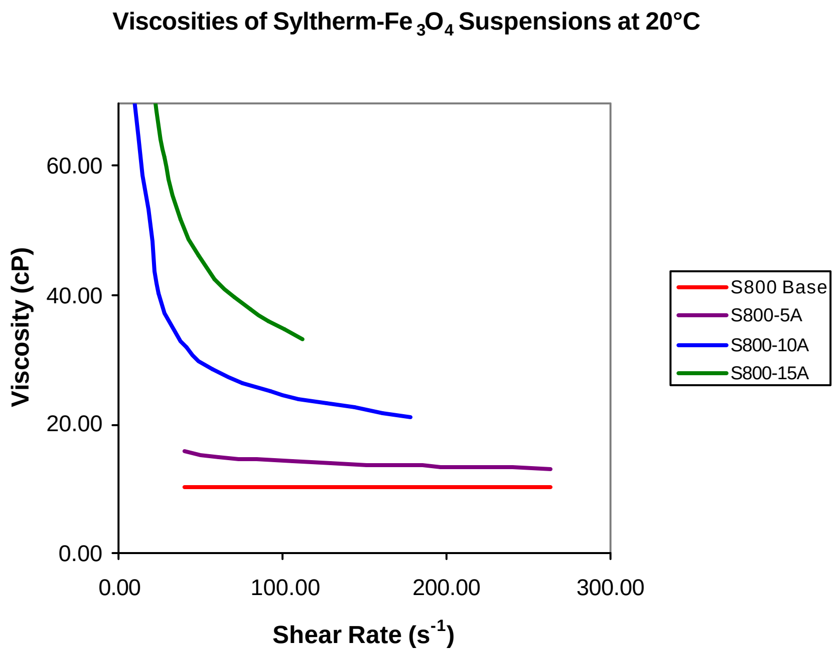

Figure 6: Rheological behavior of Syltherm - Fe_3O_4 suspensions at 20 ^{o}C.

Polyalphaolefin-based suspensions demonstrated good dispersion quality, with aggregate sizes typically ~ 300nm. Suspension stability was good to fair for all samples, with increased settling at higher loadings after extended static periods. Settled particles could be returned to the suspension with gentle agitation. Rheological behavior (**Figure 7**) of these fluids demonstrated nearly Newtonian flow characteristics at 5wt%, but became non-Newtonian at 10 and 15wt%.

Polyalphaolefin-based Suspensions at 20°C

Sample ID	**Loading**	**Aggregate Size (nm)**	**Viscosity @40s^{-1} (cP)**
PAO-B	0%	-	25.6
PAO-5A	5%	261.1	32.8
PAO-10A	10%	218.7	54.2
PAO-15A	15%	391.8	95.7

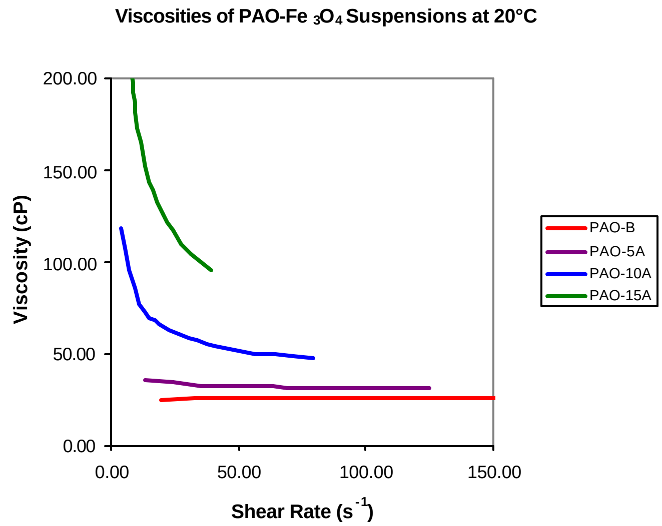

Figure 7: Rheological behavior of PAO-Fe_3O_4 suspensions at 20 °C.

C.2 Polar Nanofluids

Water-based suspensions demonstrated excellent dispersion quality, with aggregate sizes typically under 100nm. Suspension stability was also excellent, with almost no settling observed over extended static periods for 5wt%, and minor settling for 10 and 15wt%. Rheological behavior of these fluids demonstrated Newtonian flow characteristics at all loadings, **Figure** 8).

Water-based Suspensions at 20°C

Sample ID	Loading	Aggregate Size (nm)	Viscosity @260s^{-1} (cP)
AFe-B	0%	-	1.0
AFe-5	5%	116.9	1.3
AFe-10	10%	70.0	1.6
AFe-15	15%	53.9	2.1

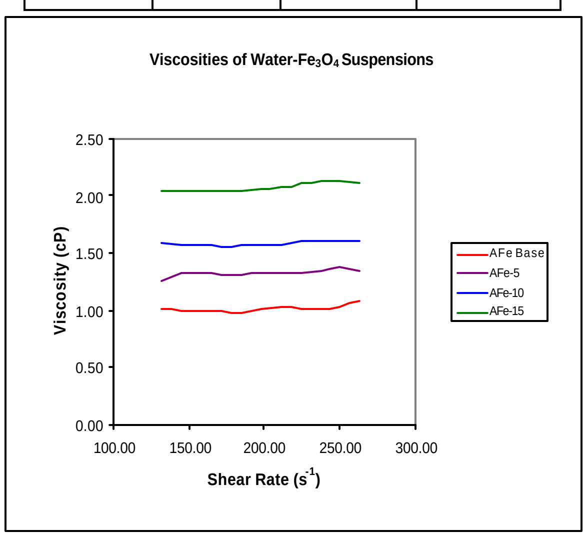

Figure 8: Rheological behavior of water –Fe_3O_4 suspensions at 20 °C.

Organic Acid Technology-based engine coolant suspensions with 50vol% water also demonstrated excellent dispersion quality, with aggregate sizes ~ 150nm. Suspension stability was good for all samples, with minor settling over extended static periods. Rheological behavior of these fluids demonstrated Newtonian flow characteristics at all loadings except 15wt%, which also exhibited an unusually large increase in viscosity (192% above the base fluid) when compared to the other samples (**Figure 9**).

OAT/Water-based Suspensions at 20°C

Sample ID	Loading	Aggregate Size (nm)	Viscosity @260s^{-1} (cP)
OAT-B	0%	-	3.8
OAT-5	5%	150.3	4.5
OAT-10	10%	152.8	5.6
OAT-15	15%	159.3	11.1

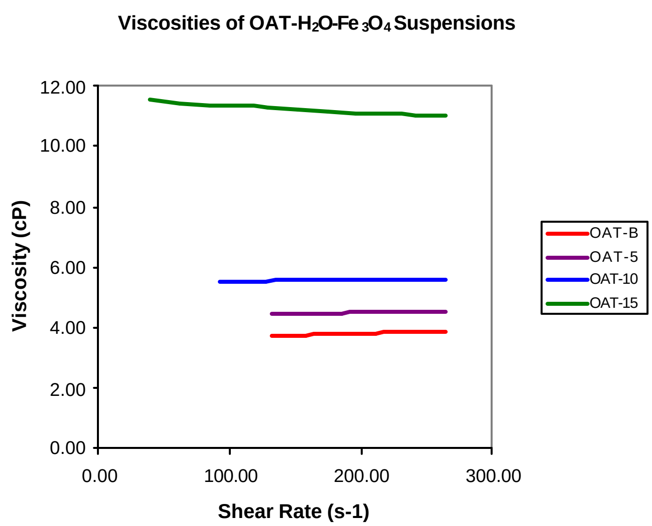

Figure 9: Rheological behavior of OAT/H_2O/Fe_3O_4 suspensions

D. Thermal Conductivity Measurements on Fe_3O_4 Dispersions

D.1 Experimental Procedure

Thermal conductivity and thermal diffusivity of our fluids was measured using a Decagon KD2 Thermal Properties Analyzer based on single needle heat pulse technique. For a known voltage and material properties, this device computes thermal properties by monitoring the dissipation of heat from a line source. All measurements are proven precise over time, and comparisons of enhancement are made in reference to such measured values. For conductivity versus temperature measurements, a NESLAB RTE-100 refrigerated bath / circulator was used with water as the working fluid for temperatures of 10, 25 and 40 degrees Celsius.

Magnetic field on the samples was applied using two sources: permanent ceramic magnets and an iron core electromagnet with copper wire windings. Two commercial Ceramic 5 grade block magnets (residual induction of Br = 3800 Gauss) were used in parallel to induce a horizontal magnetic field on the fluid sample. A schematic illustrating how thermal conductivity measurements are made in presence of a pair of ceramic permanent magnet is shown in **Figure 10**. A 2” diameter u-shaped electromagnet was built with two layers of 24-gauge copper wire with a DC voltage supply to induce an adjustable magnetic flux to the samples. The induced magnetic field, B, for iron core electromagnet of known dimensions with copper wire windings, is

$$B = (N*I)/(C*d) \quad [10]$$

where N is the number of windings, I is the current, C is a constant for materials and dimensions, and d is the distance between two heads. This electromagnet was able to generate a magnetic field as high as 1100 Gauss. A photograph of the experimental setup for conductivity measurements under a varying magnetic field is shown in **Figure 11**. Thermal conductivity measurements were made on the samples at five points within an applied magnetic field range of up to 1100 Gauss.

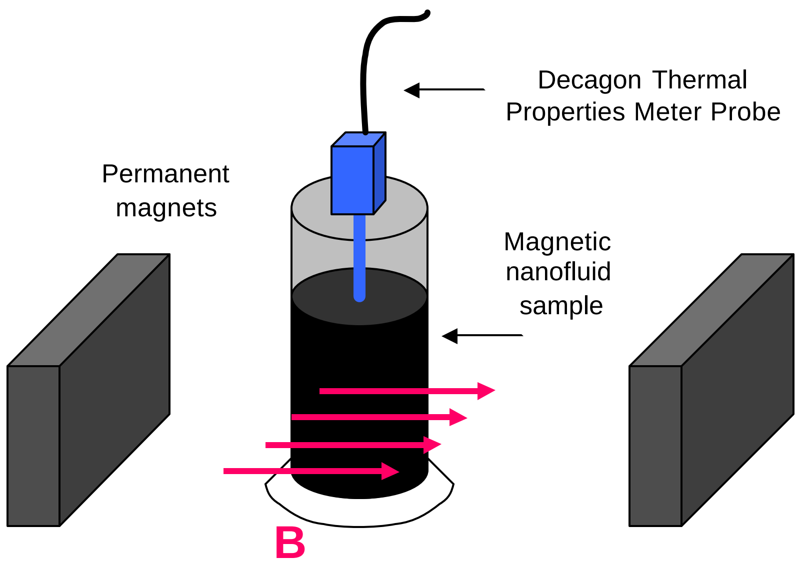

Figure 10: A schematic of the setup for measuring the thermal conductivity of magnetic nanofluids in presence of a pair of ceramic permanent magnets.

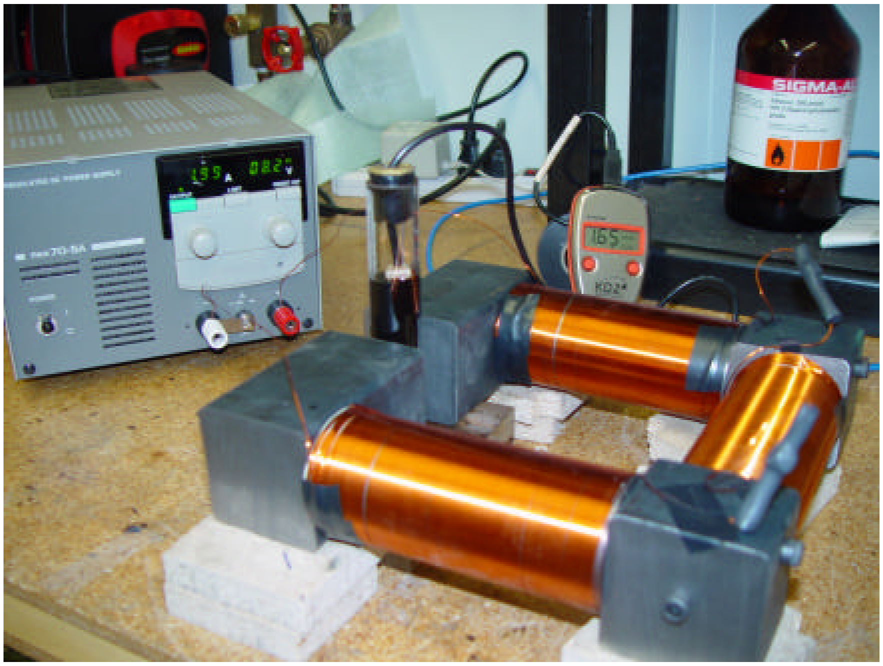

Figure 11: A photograph of the experimental setup for conductivity measurements under a varying magnetic field.

D.2 Results and Discussion

One of the objectives of the Phase I program was to determine the important parameters that can influence the thermal conductivity of the fluid. Accordingly, the nanoparticle loading in the fluids, the sample temperature, and the strength of the magnetic field were varied to understand the effect of these three parameters on the overall thermal conductivity of the fluid. Thermal conductivity measurements were done at Rutgers University, where NEI personnel worked with Rutgers researchers.

(a) Thermal Conductivity of Non-Polar Fluids <u>Without</u> an External Magnetic Field

Initially, thermal conductivity of silicone-based heat transfer fluids (Dow Syltherm) containing unmodified NEI-synthesized Fe_3O_4 nanoparticles was measured at 10, 15 and 40 ^{o}C (**Figure 12**). It was observed that thermal conductivity of these nanofluids was dependent on both nanoparticle loading and the temperature of the measurement. For three dispersions at 5, 10 and 15 wt%, there was on average 15% increase in the thermal conductivity, and a maximum increase of 17.5% occurred at 25 ^{o}C for the 15 wt% dispersion.

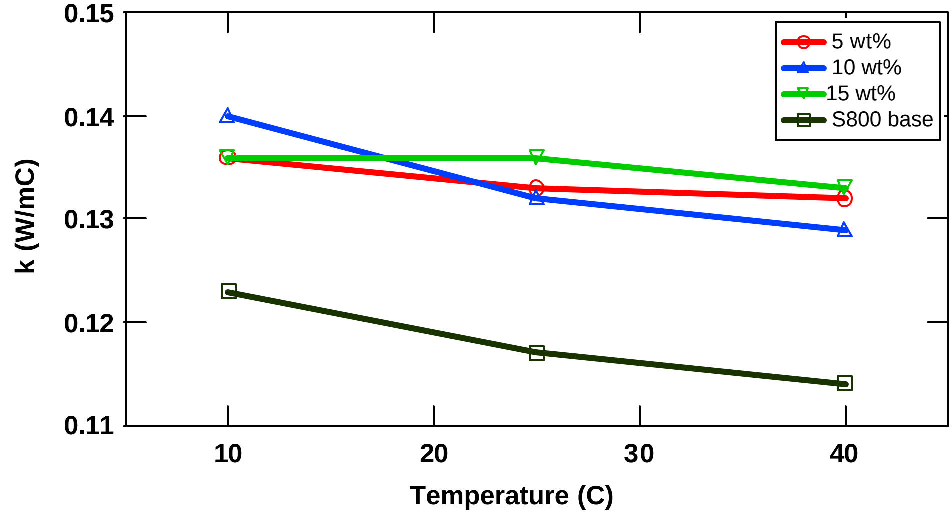

Figure 12: Thermal conductivity of Syltherm (silicone oil based heat transfer fluid) with and without unmodified Fe_3O_4 nanoparticles at three different temperatures.

As mentioned earlier, non-polar fluid dispersions containing *unmodified* Fe_3O_4 nanoparticles were unstable and had a tendency to phase separate with time. As a result, we decided to focus our study on dispersions that were synthesized using surface *modified* Fe_3O_4 nanoparticles: oleate and silicone-modified nanoparticles.

The thermal conductivity of Paratherm NF-based dispersions containing different loadings of oleate-modified Fe_3O_4 enhanced as the loading of nanoparticles was increased from 5 to 15 wt%. The 15 wt% nanoparticle fluid showed an increase of ~ 11%, while the increase was only ~ 2% in case of 5 wt% dispersion (**Figure 13**). In case of PAO- based dispersions, thermal conductivity of fluids was also a function of nanoparticle loading (**Table 1**). Adding 5wt% of Fe_3O_4 nanoparticles increased the thermal conductivity of the fluid by about 4%, while the increase in thermal conductivity was about 9% for a 15wt% nanoparticle dispersion.

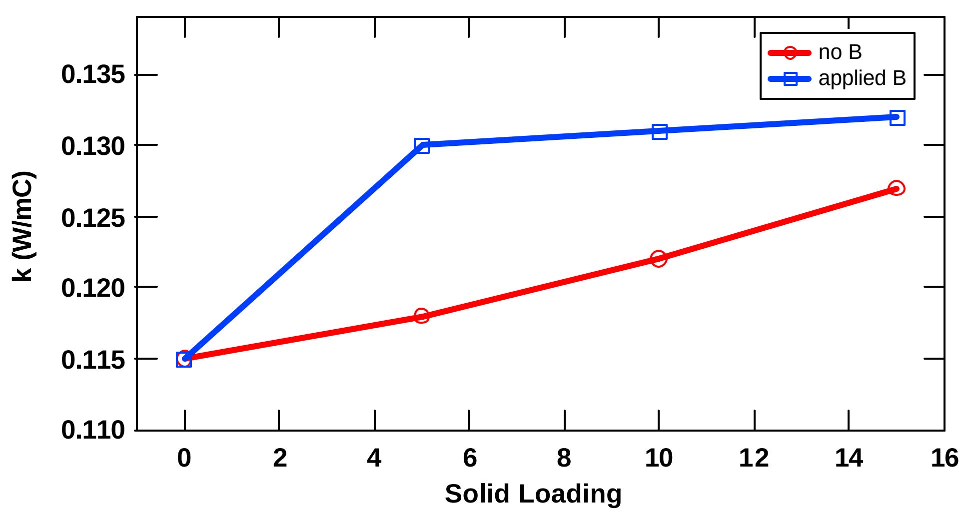

Figure 13: Thermal conductivity of Paratherm NF (hydrocarbon-based commercial heat transfer fluid) as a function of the loading of oleate-modified nanoparticles

Table 1: Thermal conductivity for PAO based dispersions with and without an induced magnetic field.

	k (W/mC) No B	% inc	**k (W/mC)** applied B	**% inc**
PAO	0.142	-	0.142	-
PAO5	0.147	3.52%	0.148	4.23%
PAO10	0.15	5.63%	0.151	6.34%
PAO15	0.153	7.75%	0.155	9.15%

Preliminarily thermal conductivity data on non-polar fluids suggested that incorporating oxide ceramic nanoparticles in commercial non-polar heat transfer fluids can enhance the overall thermal conductivity of fluids, however, the improvement was still less than 15% for a nanoparticle loading of as high as 15 wt% (~ 3 vol%), which is significantly less than what most commercial applications desire. Therefore, we explored the increase of thermal conductivity by applying an external magnetic field.

(b) Thermal Conductivity of Nanofluids With an External Magnetic Field

Thermal conductivity of a 5wt% Paratherm NF-based nanofluid increased by ~ 13% in the presence of a magnetic field (Figure 13), while the increase was only 2% for the same nanofluid in the absence of the magnetic field. Nanofluids with higher nanoparticle loading also exhibited an increasing improvement in thermal conductivity in presence of a magnetic field as compared to those observed without the magnetic field. The thermal conductivity of nanofluids in presence of a magnetic field appears to reach a maximum value and does not change further with the increase in the nanoparticle loading. The reason for such a behavior is not fully understood at the present time, and it could be a function of the surface chemistry of the nanoparticles. The Phase II program will investigate this aspect further.

Viscosity data (Figure 5) on Paratherm NF-based fluids suggest that particle surface chemistry needs to be optimized to obtain fluids with low viscosity values particularly at high nanoparticle loadings (? 10wt%). Additionally, thermal conductivity of PAO-based suspensions did not change on the application of a magnetic field. Therefore, in order to understand the full effect of an external magnetic field on thermal conductivity, we decided to make measurements on commercial oil-based ferrofluids, which exhibit a Newtonian behavior (**Figure 14**) in spite of having a large volume fraction of magnetic particles.

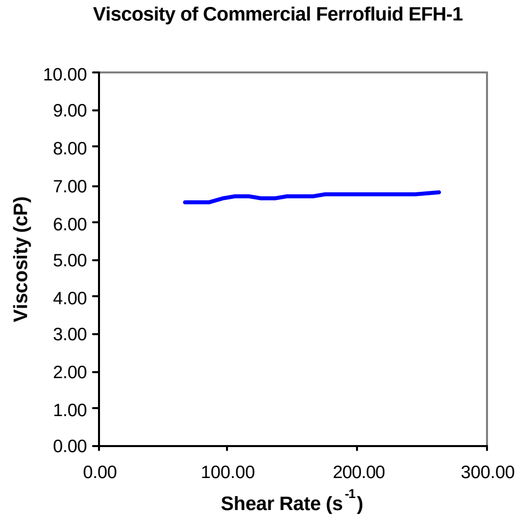

Figure 14: Viscosity of a commercial magnetic fluid as a function of the shear rate indicating a Newtonian behavior of the fluid.

It was also observed that the thermal conductivity of a magnetic fluid reaches a steady state condition with time (**Figure 15**). Initially, the thermal conductivity does not fluctuate as much as it asymptotically reaches a steady state value within 10 minutes. Fluid attains a constant thermal conductivity value, which was ~ 0.37 Wm/K for the commercial magnetic fluid. The thermal conductivity of the same fluid in the absence of the magnetic field was 0.145 Wm/K, indicating more than 150% improvement in the thermal conductivity of the fluid. These results imply that thermal conductivity of fluids can be substantially augmented if the ensemble of nanoparticles acts as a conduit for the heat flow.

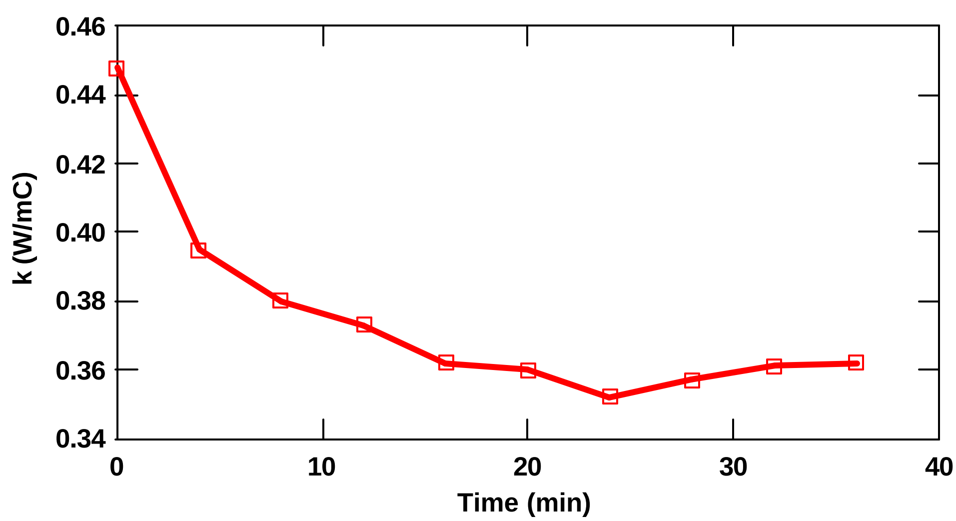

Figure 15: Thermal conductivity of a magnetic fluid (commercial ferrofluid) under the influence of an applied external magnetic field using two ceramic permanent magnets.

Thermal conductivity of this magnetic fluid increases with the increase in the magnetic field strength (**Figure 16**). Interestingly, results were similar to what was obtained with a pair of ceramic permanent magnets (B_r = 3800 Gauss), which is equivalent to a magnetic field strength of 1180 Gauss[11].

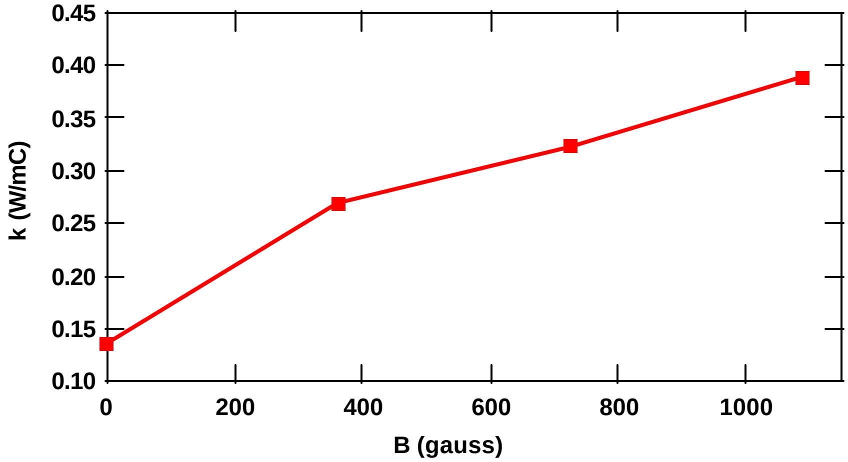

Figure 16: Thermal conductivity of a magnetic fluid as a function of the magnetic field strength.

In the light of these unexpected results and because of the significant interest from vehicle and coolant manufacturers such as Ford Motor Company, Deere & Company, and Recochem, we began developing magnetic nanofluids based on polar liquids, such as water and water/antifreeze mixture.

In case of water-Fe_3O_4 suspensions, thermal conductivity of water does not change substantially on increasing the nanoparticle loading. On the other hand, water–based nanofluids exhibit a substantial improvement in their thermal conductivity under an applied magnetic field (**Figure 17**). A 15 wt% Fe_3O_4 water suspension showed a ~ 40% increase in thermal conductivity increase under the magnetic field compared to that of without the magnetic field (**Error! Reference source not found.**). Please note that ceramic permanent magnet experiments were repeated using a different batch of fluids, and we found virtually same results, indicating that increase in thermal conductivity of water-based fluids is reproducible. OAT/water/Fe_3O_4 suspensions exhibited an interesting second order relation of conductivity with increasing solid loading, with a **maximum increase of 21%** for the 10 wt% loaded sample (**Figure 18**).

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[11] The magnetic strength of a permanent magnet with a known B_r and dimensions can be calculated from the following expression (http://www.magnetsales.com/design/designg.htm):

$$B_x = \frac{B_r}{\pi}\left(\tan^{-1}\frac{AB}{2X\sqrt{4X^2+A^2+B^2}} - \tan^{-1}\frac{AB}{2(L+X)\sqrt{4(L+X)^2+A^2+B^2}}\right)$$

where A, B and L are the magnets length, height and width, respectively, and X is the perpendicular distance.

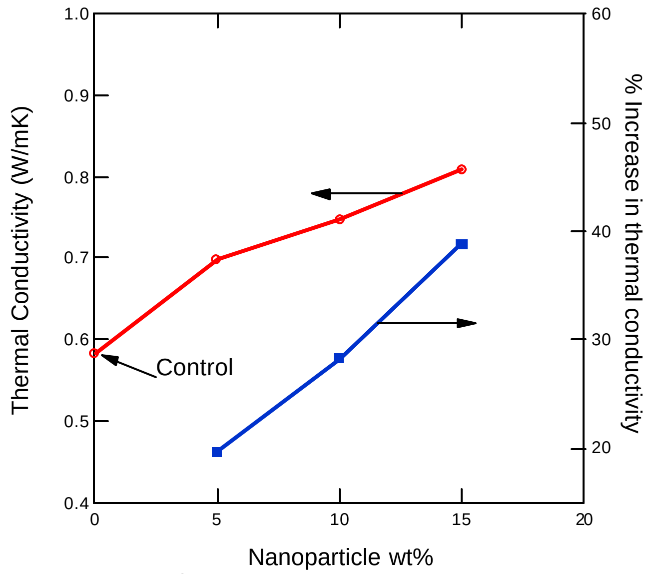

Figure 17: Thermal conductivity of NEI synthesized Fe_3O_4 water suspensions with and without a magnetic field.

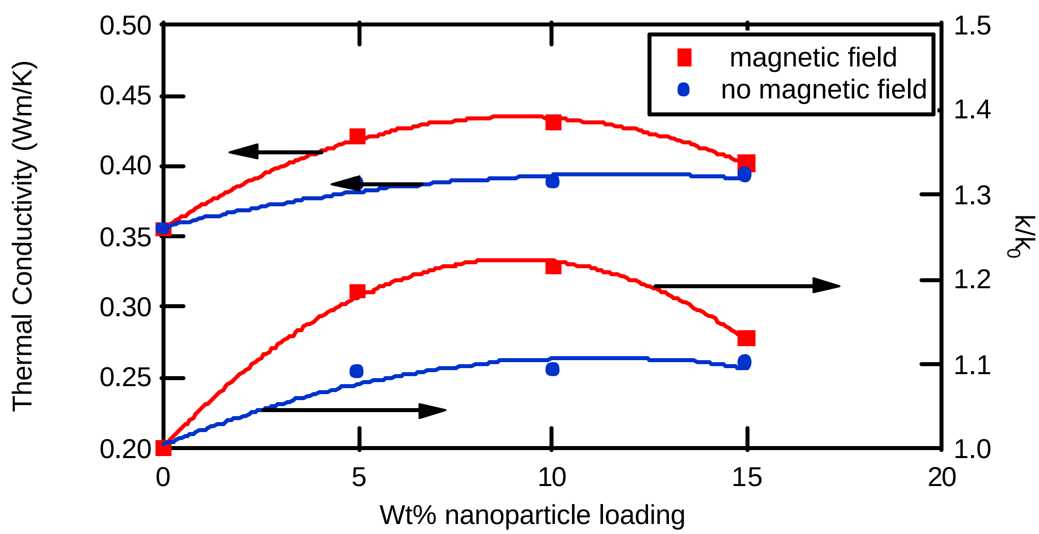

Figure 18: Thermal conductivity of OAT/H_2O/Fe_3O_4 suspensions with and without an applied magnetic field.

The difference in the thermal conductivity behavior of two polar fluids can be explained by their rheological characteristics and the quality of dispersion. In case of water, an increase in nanoparticle loading does not change the rheological behavior of fluids and the aggregate size of nanoparticles. The aggregate size for all three nanoparticle loadings was less than 100 nm, and fluids exhibited Newtonian fluid behavior without experiencing a significant change in the viscosity. On the other hand, OAT-based fluid showed a transition from a Newtonian to non-Newtonian flow pattern when the nanoparticle loading was increased from 10 to 15 wt%. Additionally, OAT-based fluids also experienced a significant increase in viscosity for the 15 wt% nanoparticle dispersion. The data suggest that the decrease in the thermal conductivity of the 15wt% OAT suspension could be the result of the relatively poor dispersion quality. Therefore, the thermal conductivity of OAT-based fluid can be further enhanced once the surface chemistry of nanoparticles dispersed in the fluid is optimized. This aspect is explained in detail in the Phase II work plan.

E. Summary of Phase I Accomplishments

In Phase I, we demonstrated that stable and economical nanofluids based on commercial heat transfer fluids can be produced without changing the intrinsic rheological properties of the base fluid. An anomalous increase in thermal conductivity of nanoparticle containing fluids was accomplished when the particle-particle interaction in the fluid was controlled, providing a good value proposition and path to commercial implementation. Specifically, what was accomplished was:

(1) Demonstrated for the first time (*to the best of our knowledge*)[12] more than 150% increase in thermal conductivity of a Nanofluid upon the application of a magnetic field, Error! Reference source not found..
(2) Formulated stable magnetic nanoparticle dispersions in water and several **commercial** heat transfer fluids such as antifreeze, Paratherm NF and PAO. PAO was provided to us by Chevron Philips, while the antifreeze was supplied by Recochem Corporation.
(3) Demonstrated that the thermal conductivity of water-based suspensions can be increased to 40% by adding only ~ 3vol% Fe_3O_4 nanoparticles, Error! Reference source not found..
(4) Measured the thermal conductivity of a variety of nanofluids, and observed that increase in the conductivity of magnetic nanofluids in presence of a magnetic field is correlated with the viscosity and the aggregate size of nanoparticles in the dispersion, indicating that thermal conductivity of fluids can be further enhanced by optimizing the surface chemistry of nanoparticles.
(5) Established several product development partnerships.

[12] There are some theoretical studies on augmenting heat transfer in magnetic fluids (by R. Ganguly, S. Sen and I. K. Puri, J. Magnetism and Magnetic Materials, vol. 271, 63 (2004)), but no practical consideration to improving the thermal conductivity has been given