Nanofluid Application in LNG Process Heat Exchange Systems

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Abstract

Improving the efficiency of heat exchange systems for liquefied natural gas (LNG) processing by using nanofluids has the potential to reduce heat transfer equipment costs and allow increases in overall heat load transfer. Nanofluids are fluids that contain particles less than 100nm in size and have been shown in several prior studies to display enhanced thermal conductivities and heat transfer coefficients. The objectives of this study are to characterize graphene and Al_2O_3 *nanofluids and to measure thermal properties and stability. The heat transfer coefficient of the nanofluids were measured by pumping each sample through copper piping submerged in a hot water bath at 50°C and measuring the outlet temperature change compared to deionised (DI) water. Results showed 0.05 vol. % reduced graphene oxide in DI water gave a 17% enhancement in heat transfer coefficient and 6 vol. %* Al_2O_3 *gave a 27% enhancement compared to DI water. Stability testing indicates graphene nanofluids are not stable when exposed to shearing conditions based on a reduction in heat transfer coefficient. Nanofluid thermal properties were used to construct heat exchanger designs to assess any reduction in size compared to using DI water. No significant change in the heat exchanger size was seen using nanofluid thermal properties due to the lubrication oil having 90% of the resistance to heat transfer.*

1. Introduction

With increasing energy costs and limited space for heat exchange equipment on offshore oil and gas processing platforms there is a need to develop more efficient heat transfer systems. Once designed and built the heat load capacity for a given heat exchanger is set within its design specifications. Potential benefits of nanofluid application in liquefied natural gas (LNG) process cooling and heating include: reduced equipment costs (CAPEX), increased heat transfer for debottlenecking and reduced pumping costs (OPEX).

Increasing the heat load of a heat exchanger can be achieved by increasing either the overall heat transfer coefficient, the size of the heat exchanger and/or fluid temperature difference. The temperature difference is typically limited by the process fluid properties and an increase in heat exchanger size is undesirable due to increased CAPEX. Increased equipment footprint is also less feasible for floating liquefied natural gas systems and current projects with plot space limitations.

Increasing the overall heat transfer coefficient of a heat exchanger can be achieved by increasing the heat transfer coefficient of the cooling/heating medium. One potential way of doing this is through the addition of nano-sized (<100nm) particles to form what are known as nanofluids (Choi & Eastman, 1995). The first study to investigate the thermal properties of nanofluids reported a 30% increase in thermal conductivity with 4.3 volumetric % (vol. %) Al_2O_3 in deionised (DI) water (Masuda, 1993).

Whilst the thermal conductivity is an important property to consider for heat transfer, it is the heat transfer coefficient that is most relevant for industrial heat exchange systems. The heat transfer coefficient is known to vary depending on flow regime, flow geometry, thermal boundary condition, flow region and thermophysical properties of the fluid (Huminic & Huminic, 2012). Studies have reported 27% enhancement of heat transfer coefficient with 6% Al_2O_3 in water and 12% increase with 1.1 vol. % Ti in water under laminar flow (He *et al.*, 2007, Rea *et al.*, 2009). Enhancements have been shown to depend on nanoparticle size, shape, chemical structure, temperature, concentration, flow velocity and method of preparation (Huminic & Huminic, 2012).

Graphene has attracted a lot interest in recent years due to its remarkable thermal properties including very high thermal conductivity measured up to 5300 W/m.K (Balandin *et al.*, 2008) compared to water with 0.6 W/m.K at room temperature. Graphene is a two dimensional monatomic thick carbon allotrope that when stacked together forms graphite (Kuila *et al.*, 2012). Graphene is commonly produced through oxidation of graphite via Hummer's method that is then exfoliated to form single-layered graphene (Kuila *et al.*, 2012).

The use of nanofluids is still a relatively new concept and the tangible benefits of their use in industrial heat transfer devices is yet to be established. The main aim of this study is to assess the potential advantages of nanofluids in LNG process cooling and heating that are expected through heat transfer enhancements. The main objectives of this project include:

1) Characterizing selected nanofluids (particle size and chemical structure).
2) Measuring nanofluid thermal properties and stability (heat transfer coefficient, specific heat capacity, thermal conductivity).
3) Designing heat exchangers based on nanofluid thermal properties.

2. Process

2.1 Nanofluid Preparation & Characterisation

Three types of nanofluids were prepared:

1) Al_2O_3 in DI water at 6, 3 and 1.5 vol. %.
2) Graphene oxide (GO) in DI water at 0.05 vol. %.
3) An initial sample of 0.05 vol. % reduced graphene oxide (r-GO) in DI water was prepared with five hours ultrasonication. A second batch was prepared with twelve hours ultrasonication at 0.05 and 0.01 vol. %.

The following equipment was used for nanofluid characterization:

- JEOL 2100 TEM - Transmission Electron Microscope (TEM) imaging.

- WITec alpha RA+ - Atomic Force Microscope (AFM).
- Malvern Zetasizer Nano ZSP - Dynamic light scattering (DLS) analysis.
- Perkin Elmer Spectrum One Spectrometer - Fourier transform infra-red (FT-IR) analysis.

2.2 Heat Transfer Coefficient Experiment

The heat transfer coefficient of the different nanofluids was measured by pumping them through a copper pipe submerged in a hot water bath at 50°C. The inlet and outlet temperature difference was measured at a constant fluid velocity in the laminar regime (Reynolds number 700-1000). Eight to ten runs were completed to obtain average readings for each fluid. Pressure drop was measured using a Deltabar S PMD70 differential pressure gauge. Enhancements in heat transfer coefficient were measured by running DI water experiments before each nanofluid and comparing the difference to account for fouling effects. Current stability tests include stirring the nanofluid samples in a beaker at a shear rate of $900s^{-1}$ which is equivalent to the shear rates in the tubes of an industrial heat exchanger.

2.3 Heat Exchanger Design

A datasheet supplied by the client for a lubrication oil heat exchanger using tempered water as the cooling medium was used to construct a base design using DI water properties, which was then compared with designs using nanofluids. Changes in nanofluid properties are shown in Table 1 with changes in graphene specific heat capacity and density values being very small.

	Al_2O_3		Graphene	
Concentration (vol. %)	2	5	0.01	0.05
Thermal conductivity (k)	16	28	11	38
Viscosity (μ)	17	36	3	13
Specific heat capacity (c_p)	-6	-14	-0.02	-0.11
Density (ρ)	5	14	0.02	0.08

Table 1 Percentage (%) change, relative to water, in thermal properties of graphene and Al_2O_3 nanofluids used for the heat exchanger design.

The well known Kern's method (Kern, 1950) was used to construct the initial heat exchanger designs and Aspen Exchanger Design and Rating (EDR) software was utilised for a second set of designs, allowing a comparison between the two design methods.

3. Results and Discussion

3.1 Nanofluid Characterization

TEM images of Al_2O_3 particles (not shown) gave particle sizes of approximately 50-250nm. DLS analysis of freshly prepared Al_2O_3 samples with average particle size diameter of 360nm decreased to 200nm after twelve hours due to gravitational settling. This result signifies the need to consider agitation mechanisms for Al_2O_3 nanofluids if used for industrial applications.

Figure 2a shows AFM profiles of r-GO particles from the first r-GO nanofluid with five hours ultrasonication, which are approximately 12nm thick. This is much larger than the second r-GO nanofluid that was prepared with twelve hours of ultrasonication having particles ~0.6nm thick (Figure 2b). From this result it can be seen that ultrasonication is important for dispersing graphene particles.

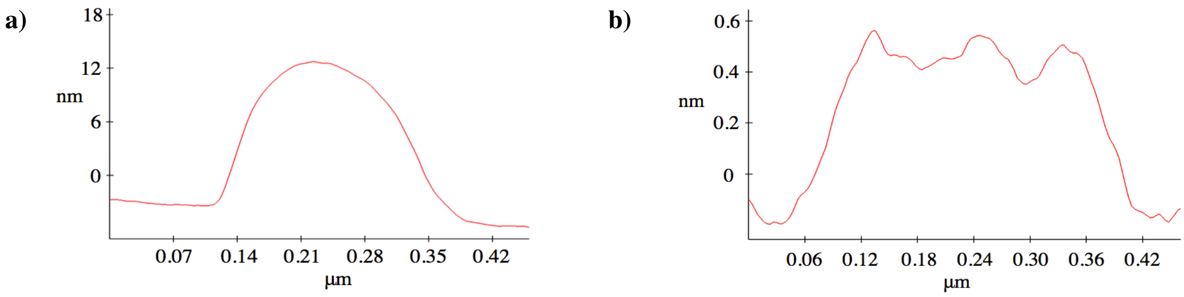

Figure 2 AFM particle profiles of:
a) Reduced Graphene Oxide - ultrasonicated for 5 hours.
b) Reduced Graphene Oxide - ultrasonicated for 12 hours.

The FT-IR analysis (Figure 3) shows that GO has a high level of oxide functionality, which acts to thermally insulate these particles (Kuila *et al*., 2012). Reduction of GO is carried out to regain some of the thermal conductivity lost due to the oxide layer (Kuila *et al*., 2012). Low oxide functionality is indicated for r-GO, which is expected to result in higher thermal conductivity of these particles and associated nanofluid (Li *et al*., 2008).

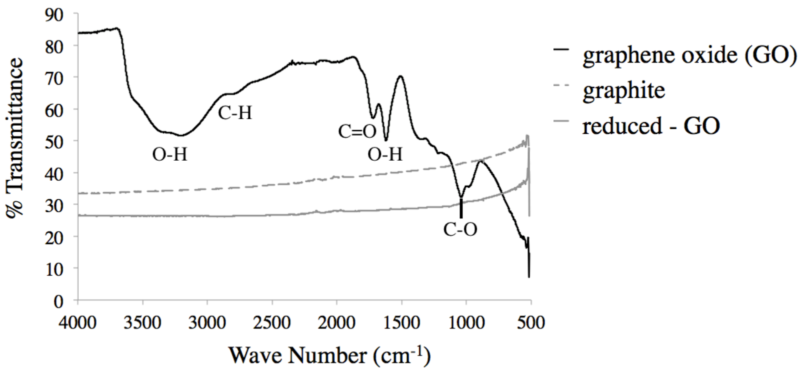

Figure 3 FT-IR analysis of graphene oxide, reduced graphene oxide and graphite.

3.2 Heat Transfer Coefficient Experiment

Figure 4a shows that 0.05 vol. % addition of GO to DI water reduced the heat transfer coefficient compared to pure DI water. While the 0.05 vol. % r-GO and 6 vol. % Al_2O_3 samples gave 17% and 27% enhancements respectively. The higher heat transfer enhancement of the r-GO was due to the low oxide functionality compared to the GO.

The heat transfer coefficient enhancement of the first r-GO nanofluid gave no change compared to DI water. The second batch (denoted by *) gave significant enhancements as a result of longer ultrasonication time leading to better separation of the graphene particles as shown by the AFM images. There was a decrease in the heat transfer coefficient enhancement for the r-GO 0.05 vol. % after being exposed to shear rates for one week. This was a significant result because it shows that this nanofluid is not stable under shearing conditions, however further stability assessments are ongoing to confirm this result.

Figure 4b illustrates the pressure drop for the different nanofluids. The GO samples gave a higher pressure drop compared to DI water whereas the r-GO and Al_2O_3 samples showed either no pressure drop or slightly lower pressure drop. This is an important consideration when assessing the pumping power requirement for different nanofluids. Studies have shown reductions in heat transfer efficiency due to higher pressure drop (Meriläinen *et al*., 2013).

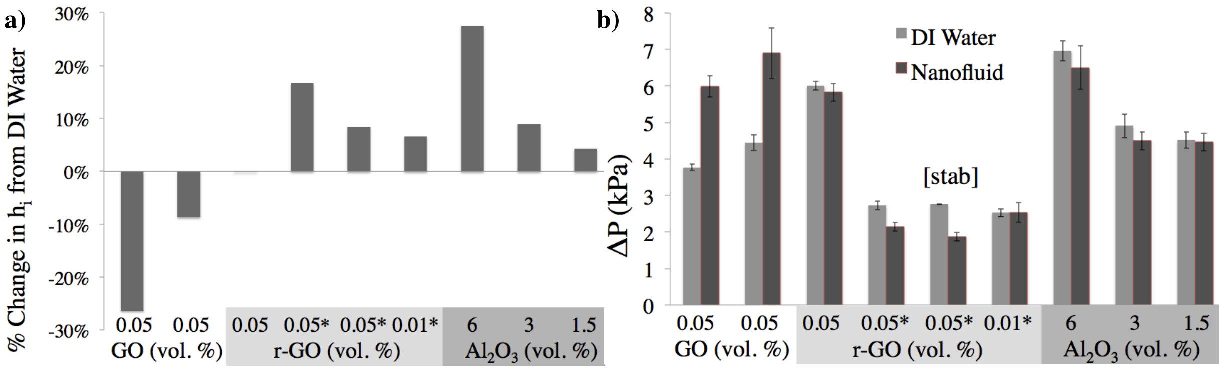

Figure 4 ***Samples ultrasonicated for 12 hours & 30% slower flow rate.**
[stab]: samples sheared at 900s^{-1} for 1 week.
a) Heat transfer coefficient (h_i) enhancement of nanofluids vs. DI water.
b) Nanofluids & DI water pressure drop (error bars - 95% confident interval).

3.3 Heat Exchanger Design

The original datasheet had 382 tubes which was higher than Kern's method that gave approximately 324 tubes and Aspen EDR that gave 290 (Table 2). The large difference is expected to be due to overdesign allowances and different design correlations. The lubrication oil made up 90% of the total resistance compared to the tempered water which made up 5%. For this reason, nanofluids did not have a large impact on heat exchanger size.

	Fluid	DI Water	Al_2O_3		Graphene	
	Vol. %	-	2	5	0.01	0.05
Kern's method	h_i (W/m^2.°C)	11,500	12,200	13,300	12,000	12,900
	Number of tubes	324	324	322	324	322
Aspen EDR	h_i (W/m^2.°C)	11,300	11,800	12,900	11,200	11,100
	Number of tubes	290	290	290	290	290

Table 2 **Internal heat transfer coefficients (h_i) and number of tubes calculated for DI water, Al_2O_3 and graphene nanofluids.**

4. Conclusions and Future Work

The work completed so far has found that when prepared properly, reduced graphene oxide and Al_2O_3 nanofluids show heat transfer enhancements compared to DI water. The thermal properties of reduced graphene oxide nanofluids have been shown to be strongly dependent on preparation technique. Initial stability assessments indicate that the heat transfer enhancement of reduced graphene oxide nanofluids are not stable after being exposed to prolonged periods of shearing. This has implications for the application of graphene nanofluids in heat exchange systems where fluids are continually circulated through pumps, pipe networks and heat exchangers. Further work will focus on assessing the stability of reduced graphene oxide nanofluids. Chemical and particle size analysis will indicate if this is due to oxidation of the graphene particles and/or changes in particle size.

The use of nanofluids had no significant effect on the heat exchanger design provided due to the fact that 90% of the resistance to heat transfer was in the hot lubrication oil compared to 5% for the cooling medium. The next stage of work will assess the impact of nanofluids on heat exchangers where there is a more even distribution of heat transfer resistance.

Based on the work completed so far it is believed that nanofluids should be considered for use in LNG process cooling and heating systems. Future work should focus on further study of nanofluid stability under shear and fluid circulation to simulate industrial conditions. Investigation of non-aqueous nanofluids such as refrigerants (Ozturk *et al.*, 2013), which offer higher graphene nanofluid stability is also warranted.

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6. References

Balandin, A. A., Ghosh, S., Bao, W., Calizo, I., Teweldebrhan, D., Miao, F. & Lau, C. N. 2008. Superior thermal conductivity of single layer graphene. *Nano Letters,* 8**,** 902-907.

Choi, S. U. S. & Eastman, J. A. 1995. Enhancing thermal conductivity of fluids with nanoparticles *Developments and Applications of Non-Newtonian Flows. FED,* 231**,** 99-105.

He, Y., Jin, Y., Chen, H., Ding, Y., Cang, D. & Lu, H. 2007. Heat transfer and flow behaviour of aqueous suspensions of TiO2 nanoparticles (nanofluids) flowing upward through a vertical pipe. *International Journal of Heat and Mass Transfer,* 50**,** 2272-2281.

Huminic, G. & Huminic, A. 2012. Application of nanofluids in heat exchangers: A review. *Renewable and Sustainable Energy Reviews,* 16**,** 5625-5638.

Kern, D. 1950. *Process Heat Transfer*, McGraw Hill.

Kuila, T., Bose, S., Mishra, A. K., Khanra, P., Kim, N. H. & Lee, J. H. 2012. Chemical functionalization of graphene and its applications. *Progress in Materials Science,* 57**,** 1061-1105.

Li, D., Muller, M. B., Gilje, S., Kaner, R. B. & Wallace, G. G. 2008. Processable aqueous dispersions of graphene nanosheets. *Nat Nanotechnol,* 3**,** 101-5.

Masuda, H. 1993. Change of viscosity and thermal conductivity of the liquid by ultrafine particle dispersion. *Netsu Bussei (Japan Journal of Thermophysical Properties),* 7**,** 227.

Meriläinen, A., Seppälä, A., Saari, K., Seitsonen, J., Ruokolainen, J., Puisto, S., Rostedt, N. & Ala-Nissila, T. 2013. Influence of particle size and shape on turbulent heat transfer characteristics and pressure losses in water-based nanofluids. *International Journal of Heat and Mass Transfer,* 61**,** 439-448.

Ozturk, S., Hassan, Y. A. & Ugaz, V. M. 2013. Graphene-enhanced nanorefrigerants. *Nanoscale,* 5**,** 541-7.

Rea, U., McKrell, T., Hu, L.-w. & Buongiorno, J. 2009. Laminar convective heat transfer and viscous pressure loss of alumina–water and zirconia–water nanofluids. *International Journal of Heat and Mass Transfer,* 52**,** 2042-2048.