Engineering Nanofluids for Heat Transfer Applications

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Cover illustration:

Schematic of NFs system as a three phase suspension system

تقدیم به :

همه اعضای خانواده ام

مخصوصا همسر صبور و مهربانم که بدون همراهی، گذشت، تحمل و بردباری ایشان طی این مسیر برایم مقدور نبود

و به فرزند عزیزم: محمد طه

فروتنانه از همه زحمات شما تشکر میکنم.

Abstract

Nanofluids (NFs) are nanotechnology-based colloidal dispersion prepared by dispersing nanoparticles (NPs) in conventional liquids, as the base liquid. These advanced fluids have displayed potential to enhance the performance of conventional heat transfer fluids. This work aims at providing an insight to the field of NFs by investigating in detail the fabrication and evaluation of physico-chemical, thermo-physical and heat transfer characteristics of NFs for practical heat transfer applications. However, in order to utilize NFs as heat transfer fluids in real applications there are some challenges to overcome. Therefore, our goal is not only to optimize the thermo-physical properties of NFs with the highest thermal conductivity (TC) and minimal impact of NPs on viscosity, but also on preparing NFs with good stability and the best heat transfer performance. In the first stage, detailed studies were carried out to engineer NFs with good stability and optimal thermo-physical properties. In this work we investigated the most important factors, and the dependence of thermo-physical properties of NFs, including NP composition and concentration, NF stability, surface modifiers, particle size (NP size and particle with micron size), NF preparation method (two-step vs one-step method) and base liquid was studied. We also demonstrated, for the first time, the role of crystal structure, exemplified by alpha- and beta- SiC particles, on thermo-physical properties of NFs. For these purposes several NFs were fabricated using different nanostructured materials and various base liquids by one-step and two-step methods. An optimization procedure was designed to keep a suitable control in order to reach the ultimate aim where several stages were involved to check the desired characteristics of each NF system. Among several NFs systems studied in the first stage evaluation, a particular NF system with 9 wt% concentration, engineered by dispersing SiC NPs with alpha- crystal structure in water/ethylene glycol as based liquid exhibited the optimal thermo-physical properties. This NF was the only case which could pass the all criteria involved in the optimization procedure by exhibiting good stability, TC enhancements of ~20% with only 14% increase in viscosity at 20 $^{\circ}$C. Therefore, this engineered NF was considered for next phase evaluation, where heat transfer coefficient (HTC) tests were designed and carried out to evaluate the thermal transport property of the selected alpha- SiC NF. A HTC enhancement of 5.5% at equal pumping power, as realistic comparison criteria, was obtained indicating the capability of this kind of NFs to be used in industrial heat transfer applications. These findings are among the few studies in the literature where the heat transfer characteristics of the NFs were noticeable, reproducible and based on a realistic situation with capability of commercializing as effective heat transfer fluid.

Keywords: nanofluid, thermal conductivity, viscosity, heat transfer, heat transfer coefficient, HTC, SiC nanoparticles, Cu nanoparticles, mesoporous silica, CNT, microwave synthesis

List of papers included in the thesis:

1. **Nader Nikkam**, Mohsin Saleemi, Muhammet S. Toprak, S. Li, Mamoun Muhammed, Ehsan B. Haghighi, Rahmatollah Khodabandeh, and Björn Palm, "Novel Nanofluids Based on Mesoporous Silica for Enhanced Heat Transfer", Journal of Nanoparticle Research, 2011,13, 6201-6206

2. Ehsan B. Haghighi, **Nader Nikkam**, Mohsin Saleemi, Mohammadreza Behi, Seyed A. Mirmohammadi, Heyko Poth, Rahmatollah Khodabandeh, Muhammet S. Toprak, M. Muhammed and Björn Palm, "Shelf Stability of Nanofluids and Its Effect on Thermal Conductivity and Viscosity", Measurement Science and Technology, 2013, 24, 105301-105301-11

3. Sathya P. Singh, **Nader Nikkam**, Morteza Ghanbarpor, Muhammet S. Toprak, Mamoun Muhammed and Rahmatollah Khodabandeh, "Design and Evaluation of Carbon Nanotube Based Nanofluids for Heat Transfer Applications", Materials Research Society, Proceedings of the Symposium on Nanoscale Heat Transport—From Fundamentals to Devices, 2013, 1543, 143-148

4. **Nader Nikkam**, Morteza Ghanbarpor, Mohsin Saleemi, Muhammet S. Toprak, Mamoun Muhammed and Rahmatollah Khodabandeh, "Thermal and rheological properties of micro- and Nanofluids of copper in diethylene glycol – as heat exchange liquid", Materials Research Society, Proceedings of the Symposium on Nanoscale Heat Transport—From Fundamentals to Devices, 2013, 1543, 165-170

5. **Nader Nikkam**, Morteza Ghanbarpour, Mohsin Saleemi, Ehsan B. Haghighi, Rahmatollah Khodabandeh, Mamoun Muhammed, Björn Palm and Muhammet S. Toprak, "Experimental investigation on thermo-physical properties of copper/diethylene glycol nanofluids fabricated via microwave-assisted route", Applied Thermal Engineering, 2014, 65, 158-165

6. **Nader Nikkam**, Mohsin Saleemi, Ehsan B. Haghighi, Morteza Ghanbarpour, Rahmatollah Khodabandeh M. Muhammed, Björn Palm and Muhammet S. Toprak, "Fabrication, characterization and thermo-physical property evaluation of water/ethylene glycol based SiC nanofluids for heat transfer applications", Nano-Micro Letters, 2014, 6, 178-189

7. **<u>Nader Nikkam</u>**, Ehsan B. Haghighi, Mohsin Saleemi, Mohammadreza Behi, Rahmatollah Khodabandeh, Mamoun Muhammed, Björn Palm and Muhammet S. Toprak, "Experimental Study on Preparation and Base Liquid Effect on Thermo-physical Characteristics of α-SiC Nanofluids", 2014, *In Press* in the International Communications in Heat and Mass Transfer

Other work not included in this thesis:

1. Ehsan B. Haghighi, Mohsin Saleemi, **<u>Nader Nikkam</u>**, Rahmatollah Khodabandeh, Muhammet S. Toprak, Mamoun Muhammed and Björn Palm, "Cooling performance of nanofluids in a small diameter tube", Experimental Thermal and Fluid Science, 2013, 49, 114–122

2. Ehsan B. Haghighi, Mohsin Saleemi, **<u>Nader Nikkam</u>**, Rahmatollah Khodabandeh, Muhammet S. Toprak, Mamoun Muhammed, Björn Palm, "Accurate basis of comparison for convective heat transfer in nanofluids" International Communications in Heat and Mass Transfer, 2014, 52, 1-7

3. Sadegh Motahar, **<u>Nader Nikkam</u>**, Ali A. Alemrajabi, Rahmatollah Khodabandeh, Muhammet S. Toprak and Mamoun Muhammed, " A novel phase change material containing mesoporous silica nanoparticles for thermal storage: a study on thermal conductivity and viscosity", International communications in Heat and Mass Transfer, 2014, Accepted Manuscript

4. Morteza Ghanbarpour, **<u>Nader Nikkam</u>**, Rahmatollah Khodabandeh, Muhammet S. Toprak, "Experimental study of nanofluid effect on thermal performance of screen mesh heat pipe", Proceedings of the 13 UK Heat Transfer Conference UKHTC2013, 2013, 98-1- 98-8

5. Morteza Ghanbarpour, **<u>Nader Nikkam</u>**, Rahmatollah Khodabandeh, Muhammet S. Toprak, M. Muhammed and Björn Palm, "Thermal performance of screen mesh heat pipe with Al_2O_3 Nanofluid", Submitted Manuscript

6. Mariam Jarahnejad, Ehsan B. Haghighi, Mohsin Saleemi, **<u>Nader Nikkam</u>**, Rahmatollah Khodabandeh, Björn Palm, Muhammet S. Toprak and Mamoun Muhammed,"The Experimental investigation of effective parameters on viscosity of water based Al_2O_3 and TiO_2 nanofluids", Submitted Manuscript

7. Peter Krajnik, Amir Rashid, F. Pušavec, M. Remškar, **<u>Nader Nikkam</u>** and Muhammet S. Toprak, "Developments and innovation-based breakthrough possibilities for integration of nanotechnology into manufacturing technologies", Manuscript

Conference Presentations:

1. Sadegh Motahar, **Nader Nikkam**, Ali Akbar Alemrajabi, Rahmatollah Khodabandeh and Muhammet S. Toprak, *"Experimental and Theoretical Investigation on Thermal Conductivity of Multiwalled Carbon Nanotubes Dispersed n-Octadecane as a Phase Change Material"*, 4th International conference on nanostructures, ICNS4, March 6-9, 2014, Kish Island, Iran

2. Morteza Ghanbarpour, **Nader Nikkam**, , Rahmatollah Khodabandeh, Muhammet S. Toprak, Mamoun Muhammed, *"Experimental study of nanofluid effect on thermal performance of screen mesh heat pipe"*, UK Heat Transfer Conference, September 2-4, 2013, London, UK

3. Ehsan B. Haghighi, Morteza Ghanbarpour, Mohsin Saleemi, **Nader Nikkam**, Rahmatollah Khodabandeh, Muhammet S. Toprak, Mamoun Muhammed and Björn Palm, *"Measurement of temperature-dependent viscosity of nanofluids and its effect on pumping power in cooling systems"*, International Conference on Applied energy, ICAE2013, July 1-4, 2013, Pretoria, South Africa

4. **Nader Nikkam**, Mohsin Saleemi, Ehsan B. Haghighi, Morteza Ghanbarpour, Muhammet S. Toprak, Rahmatollah Khodabandeh, Mamoun Muhammed and Björn Palm Design and Fabrication of Efficient Nanofluids Based on SiC Nanoparticles for Heat Exchange Applications, European Materials Research Conference, EMRS, May 27-31, 2013, Strasbourg, France

5. Mohsin Saleemi, **Nader Nikkam**, Milad G. Yazdi, Muhammet S. Toprak and M. Muhammed, *"Effect of particles size and surface modification on thermal conductivity and viscosity of alumina nanofluids"* European Materials Research Conference, EMRS, May 27-31, 2013, Strasbourg, France

6. **N. Nikkam**, Morteza Ghanbarpour, Muhammet S. Toprak, Mamoun Muhammed and Rahmatollah Khodabandeh, *"Thermal and rheological properties of micro- and Nanofluids of copper in diethylene glycol – as heat exchange liquid"*, Materials Research Society Conference, Materials Research Society Conference, MRS, April 1-5, 2014, San Francisco, USA

7. **Nader Nikkam**, Sathya P. Singh, Morteza Ghanbarpour, Muhammet S. Toprak, Rahmatollah Khodabandeh and Mamoun Muhammed, *"Design and Evaluation of Carbon*

Nanotube Based Nanofluids for Heat Transfer Applications", Materials Research Society Conference, Materials Research Society Conference, MRS, April 1-5, 2014, San Francisco, USA

8. **Nader Nikkam**, Mohsin Saleemi, Ehsan B. Haghighi, Morteza Ghanbarpour, Muhammet S. Toprak, Rahmatollah Khodabandeh, Mamoun Muhammed and Björn Palm, *"Nano‑engineered SiC Heat Transfer Fluids for Effective Cooling"*, Materials Research Society Conference, Materials Research Society Conference, MRS, April 1-5, 2014, San Francisco, USA

9. Ehsan Bitaraf Haghighi, M. Ghadamgahi, Mohammadreza Behi, Seyed A. Mirmohammadi, Rahmatollah Khodabandeh, Björn Palm, Mohsin Saleemi, **Nader Nikkam**, Muhammet S. Toprak and Mamoun Muhammed, *"Measurement of temperature-dependent viscosity of nanofluids and its effect on pumping power in cooling systems",* 6th European Thermal Sciences Conference (Eurotherm 2012), September 4-7, 2012, Poitiers – Futuroscope, France

10. **Nader Nikkam**, Sathya P. Singh, Mohsin Saleemi, Muhammet S. Toprak, Rahmatollah Khodabandeh, Mamoun Muhammed and Björn Palm, *"A comparative study of rheological properties and thermal conductivity of silver nanofluids in water and ethylene glycol base fluids"*, 8th Nanoscience and Nanotechnology Conference, June 25-29, 2012, Ankara, Turkey

11. **Nader Nikkam**, Mohsin Saleemi, Muhammet S. Toprak, Ehsan B. Haghighi, Rahmatollah Khodabandeh, Mamoun Muhammed and Björn Palm, *"Effect of nanoparticle morphology on thermal conductivity and rheology of Zinc Oxide nanofluids"*, European Materials Research Society Conference, EMRS, May 14-18, 2012, Strasbourg, France

12. **Nader Nikkam**, Mohsin Saleemi, Muhammet S. Toprak, Ehsan B. Haghighi, Rahmatollah Khodabandeh, Mamoun Muhammed and Björn Palm, *"Rheological Properties of Copper Nanofluids Synthesised by Using Microwave‑Assisted Method"*, 4th International conference on nanostructures, ICNS4, 12-14 March, 2012, Kish Island, Iran

13. Mohsin Saleemi, **Nader Nikkam**, Muhammet S. Toprak, Ehsan B. Haghighi, Rahmatollah Khodabandeh, Mamoun Muhammed and Björn Palm, *"One Step synthesis of Ceria (CeO_2) Nanofluids with enhanced thermal transport Properties"*, 7th Nanoscience and Nanotechnology Conference, 27 June- 1 July, 2011, Istanbul, Turkey

14. **Nader Nikkam**, Mohsin Saleemi, Muhammet S. Toprak, Ehsan B. Haghighi, Rahmatollah Khodabandeh, Mamoun Muhammed and Björn Palm, *"Microwave-assisted Synthesis of Copper Nanofluids for Heat Transfer Applications"*, 7th Nanoscience and Nanotechnology Conference, 27 June- 1 July, 2011, Istanbul, Turkey

15. Mohsin Saleemi, **Nader Nikkam**, Muhammet S. Toprak Sahnghua Li, Ehsan B. Haghighi, Rahmatollah Khodabandeh, Mamoun Muhammed and Björn Palm, *"Ceria Nanofluids for Efficient Heat Management"*, 10th International Conference on Nanostructured Materials, September 13-17, 2010, Rome, Italy

16. **Nader Nikkam**, Mohsin Saleemi, Muhammet S. Toprak Shanghua Li, Ehsan B. Haghighi, Rahmatollah Khodabandeh, Mamoun Muhammed and Björn Palm, *"Novel Nanofluids Based on Mesoporous Silica for Enhanced Heat Transfer"*, 10th International Conference on Nanostructured Materials, September 13-17, 2010, Rome, Italy

Granted patent/ patent applications:

1. Granted Patent: **Nader Nikkam**, Mohsin Saleemi, Muhammet S. Toprak, Shanghua Li and Mamoun Muhammed, "The Use of a Suspension Comprising Mesoporous Silica Particles As Heat Exchange Fluids" (Swedish Patent number: SE1000924-9), IPC (International Patent Classification): C01B33/141, C08K3/36, C09K5 /00

2. Submitted Patent Application: Mohsin Saleemi, **Nader Nikkam**, Mohammadreza Behi, Ehsan B. Haghighi, Muhammet S. Toprak, Rahmatollah Khodabandeh and Mamoun Muhammed, "Method and Apparatus for Simple Determination of The Stability of Suspensions" (Swedish patent application number: 1100961-0)

3. Submitted Patent Application: **Nader Nikkam**, Muhammet S. Toprak, Peter Krajnik and Amir Rashid, "Heat exchange Fluid Comprising Layered Structured Particles in a Base Liquid, Method of Preparation Thereof and Its Application" (Swedish patent application number: 1230064-6)

4. Submitted Patent Application: **Nader Nikkam**, Muhammet S. Toprak, P. Krajnik and Amir Rashid, "Metalworking Fluid Comprising Layered Structured Particles in a Base Liquid, Method of Preparation Thereof and Its Application" (Swedish patent application number: 1230063-8)

5. Submitted Patent Application: **Nader Nikkam**, Muhammet S. Toprak, Mamoun Muhammed, Rahmatollah Khodabandeh, Sadegh Motahar, Ali A. Alemrajabi, "Composite Comprising Phase Change Materials Enhanced with Mesoporous Particles for Enhanced Thermal Energy Storage" (Swedish patent application number: 1430026-3)

Contributions of the author

Paper 1: Planning of the experiments, preparation of NFs, performing the experiments related to the NFs/nanostructured materials, writing the manuscript.

Paper 2: Performing the experiments related to material part including materials characterization, contributed in writing the manuscript.

Paper 3: Planning of the major parts of the experiments, performing the experiments, fabrication of NFs, contributed in writing the manuscript.

Paper 4: Planning of the experiments, fabrication of NFs, performing the experiments related to NFs and nanostructured materials, material characterization, writing the manuscript.

Paper 5: Planning of the experiments, synthesis of NFs, performing the experiments related to NFs and nanostructured materials, material characterization, writing the manuscript.

Paper 6: Planning of the experiments, fabrication of NFs, performing the experiments related to NFs and nanostructured materials, material characterization, writing the manuscript.

Paper 7: Planning of the experiments, fabrication of NFs, performing the experiments related to NFs and nanostructured materials, material characterization, writing the manuscript.

Abbreviations and symbols

A	Area, m^2
Ave	Average
AR-CNT	As received carbon nanotube
bl	Base liquid
C_p	Specific heat capacity, J/kgK
CNT	Carbon nanotube
D	Pipe diameter, m
DLS	Dynamic light scattering
DW	Distilled Water
ED	Electron diffraction
eff	Effective
F	Fluid
F	Friction factor
FTIR	Fourier transform infrared
HT-CNT	Heat treated carbon nanotube
HTC	Heat transfer coefficient
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
In	Inner
K	Thermal conductivity, W/m K
L	Length, m
Out	Outer
XRD	X-ray diffraction
x^*	Dimensionless length, $(L/D_{in})/$ (Re Pr)
ṁ	Mass flow rate, kg/s
$MPSiO_2$	Mesoporous silica
MW	Microwave
NF	Nanofluid
NP	Nanoparticle
Nu	Nusselt number, h D_{in}/k
Pr	Prandtl number, (Cp μ)/k
Re	Reynolds number, $(\rho\, u_m\, Di)/\mu$
ΔP	Pressure drop, Pa
$q^{"}$	Heat flux, W/m^2
P	Pumping power, W

Q	Heat, W
T	Temperature, $^\circ$C
TC	Thermal conductivity
TGA	Thermogravimetric Analysis
THW	Transient Hot Wire
TPS	Transient Plane Source
SEM	Scanning electron microscopy
Surfactant	Molecules that can interface with both oil and water phases due to its amphiphillic structure Surface-inner
S-in	Surface-inner
S-out	Surface-outer
TEM	Transmission electron microscopy
U	Velocity, m/s
W/EG	Water/ethylene glycol mixture
X	Axial distance, m
$\dot{\forall}$	Volume flow rate, m^3/s
μ	Dynamic viscosity, cP
ϑ	Kinematic viscosity, m^2/s
ρ	Density, kg/m^3

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1. Introduction

Heat transfer is one of the most important industrial processes. In any industrial facilities heat must be efficiently managed by adding, removing or moving in the relevant sectors. Conventional heat transfer fluids such as water, ethylene glycol (EG), pumping oil, etc, have not shown sufficient capability for cooling applications due to their poor thermal performance. It has been already demonstrated that adding solid particle to these traditional fluids could enhance their thermal performance [1-2]. However, still these suspensions with micrometer or larger size particles are not efficient choice for the high-tech applications such as microelectronics, data centers and micro-channels. Therefore, development of highly efficient heat transfer fluids for solving the drawback of conventional fluids has become one of the most important priorities in the cooling industries. In last decade, nanoscience and nanotechnology (NFs) has offered new solution by introducing nanofluids (NFs) which may assist to enhance heat transfer fluids' performance especially in the high-tech applications.

1.1 Nanoscience and nanotechnology

Nanoscience is the new advanced science discussing the materials on an atomic or molecular scale by synthesis, characterization, exploration or exploitation of nanostructured materials. Nanostructured materials are defined as the materials whose structural elements - clusters, crystallites or molecules - have dimensions in the range between 1 and 100 nanometer [3]. In nanoparticles (NPs) due to the increase of surface area to the volume, some physical and chemical properties such as thermal, electrical, mechanical, chemical, optical and magnetic property of the materials can be changed significantly. The most important point is that nanostructured materials exhibit different and unique properties as compared to the bulk materials with the same compositions [4]. Basically two major approaches, as "bottom up" and "top-down" approaches are used to fabricate the nanostructured materials. In the first approach the nanoscale materials are synthesized molecule by molecule in a controlled way by using some methods such as chemical vapor deposition, solution reduction, precipitation, etc [5-6]. The top down method mostly involves the lithographic patterning techniques [7-8]. As an interdisciplinary field, nanotechnology involves chemical engineering, material science, physics and chemistry, medical science, biotechnology, energy engineering and etc [9]. In the coming decade nanotechnology will have huge impact to change and improve every part of human lives

and for this reason it has been considered one of the most important technologies in near future [10]. For instance, regarding the energy fields and application of nanotechnology in these area, nanotechnology has a great range of potential applications such energy saving, energy efficiency, energy storage and etc [11]. In this thesis NFs for heat transfer applications as one of the important applications of nanotechnology for improving energy efficiency will be discussed.

1.2 NFs and its applications

NFs are new class of solid/liquid mixtures engineered by dispersing nanometer size particles (NPs) or any nanostructures in conventional base liquids [12]. According to the literature, NPs could be metallic/intermetallic compounds (such as Ag [13], Cu [14], Ni [15], Au [16], Fe [17], etc), ceramic compounds such as oxides, sulfides and carbides. Among the ceramics, Al_2O_3 [18],, MoS_2 [19], Fe_2O_3 [20] , Fe_3O_4 [21], CuO [22], TiO_2 [23], SiO_2 [24], CeO_2 [25], ZnO [26], mesoporous SiO_2 [27] SiC [28], and WS_2 [29] are some nanostructured ceramic materials reported in the literature. Nanostructured materials can be also carbon based compounds, such as carbon nanotube [30], graphane [31], graphane oxide [32], graphite [33], etc. Base liquids are
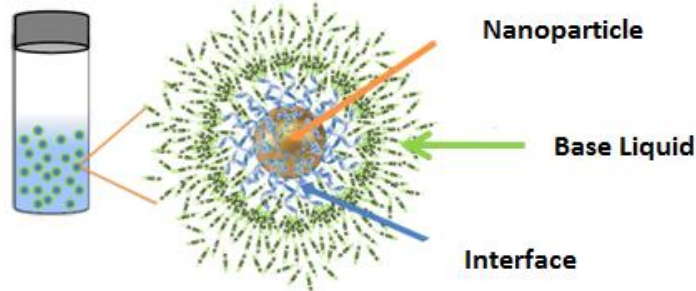
Figure1.1 Schematic of NPs dispersion systems (NFs) as a three phase suspension system

selected from water, ethylene glycol (EG), mixture of water and EG (W/EG), diethylene glycol (DEG), polyethylene glycol, engine oil [34], vegetable oil [35], paraffin [36], coconut oil [37], gear oil [38], kerosene [39], pump oil [40], etc. This new dispersion can be considered a suspension with three phase system as figure1.1 shows: solid phase (NPs), solid/liquid interface and the liquid phase. From more than a decade ago since the introduction of NF concept was originated, the potentials of NFs applications in different area have attracted increasing attention. For this reason many researchers are working in NF area for different aims and applications.

A wide range of applications for NFs in different areas such as biomedical applications, lubrication, surface coating, and petroleum industry have been reported in the literature. Figure 1.2 displays some of NFs potential applications in different areas. As literature reports NFs have been used in several biomedical and nano-medicine applications such as nanodrug delivery [41], cancer therapeutics and sensing and imaging [42] and Nano-cryosurgery [43]. For instance there are numerous applications that involve magnetic NFs such as hyperthermia, magnetic cell separations and contrast improvement in magnetic resonance imaging. [44]. About application of NFs in non-renewable energy fields such as petroleum industry, some reports can be found in the literature. For example recent experiments have exposed that some NFs have successfully been
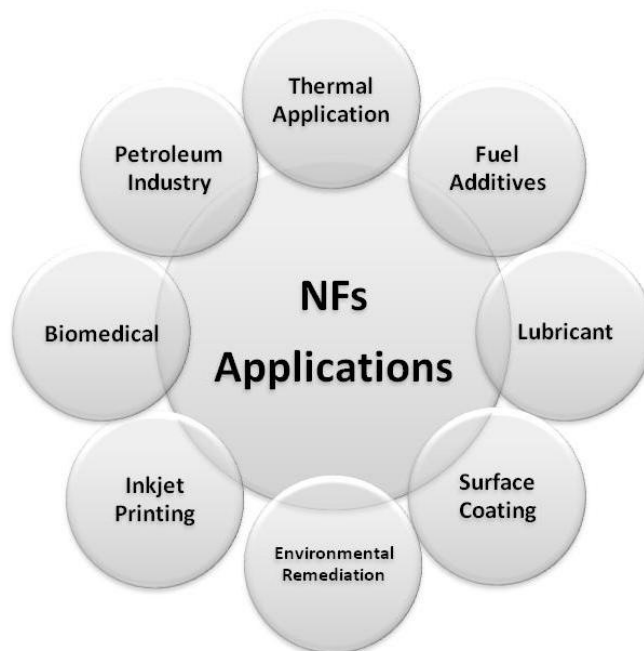
Figure 1.2 Different applications of NFs

formulated and applied in enhanced oil recovery (EOR) process [45-46], anticorrosive coatings, wettability alteration and drilling technology are other applications of NFs concerning oil and petroleum industry [47]. Recently, NFs systems prepared by dispersing NPs (such as MoS_2, TiO_2 and copper oxide) in the conventional lubricating oil have successfully enhanced as anti-wear properties and friction-reduced [48]. These features exhibit the potential of NFs' applications as effective lubricants. Several reports in the literature also show the remarkable potential of NFs for use in surface coating [49], environmental remediation (for example soil remediation) [50], inkjet printing [51] and as fuel additives [52].

1.2.1 NFs thermal applications:

Cooling is one of the most essential scientific challenges in different industries Therefore, among all applications of NFs, their potential for heat transfer applications have attracted the most attentions. [53]. Figure 1.3 shows some capability of NFs for thermal applications. NFs can be used in transport systems such as automotive and automobile radiator [54-55]. In metal processing they can be utilized in metal cutting [56-57]. They could also be used as efficient coolant in data centers and electronics cooling systems [58].
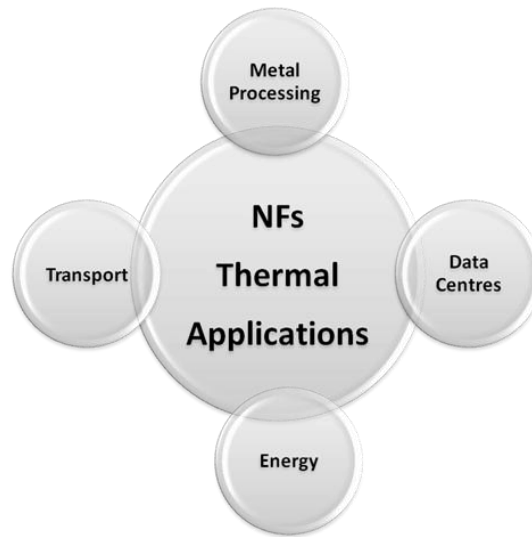
Figure 1.3 Potential of NFs for thermal application

In the literature there are some studies reporting the capability of NFs as energy storage media such as fabricating advanced phase change materials (PCM) for thermal energy storage [59] or solar absorption where NFs could enhance the absorption property of the conventional working fluid in solar collectors [60].

1.3 NFs preparation methods

It must be mentioned that, preparation of NFs is not only simple mixing and dispersing solid particles in a base liquid. It is the most significant stage in the use of NPs or any nanostructured materials to enhance the thermal characteristics of conventional heat transfer fluids. The reason is that agglomeration of solid particles could happen in base liquid media if the NFs are not prepared properly which may in turn result in poor thermo-physical property of NFs. There are

two major techniques, which are typically used for NFs preparation: two-step method and one-step (single step) method.

1.3.1 Preparation of NFs via a two-step method

In the two-step method [61-62], which is the most commonly used technique, NPs, nanotubes, nanofibers or any nanostructured materials are initially synthesized as dry powders via physical or chemical methods. After that the synthesized dry powders are dispersed in base liquids. As solid NPs/nanostructures have already been produced in industrial scale, this method is the best choice to large scale production of NFs. However, because of high surface activity of particles, agglomeration/aggregation of NPs is unavoidable. Hence, sedimentation of NPs can take place in this method, which affects the NF's properties negatively. This drawback (higher sedimentation rate of NPs in the base liquid) in the two-step method has motivated the researchers to replace this method with other technique to prepare NFs with minimum NPs agglomeration. For this reason, preparation of NFs using one-step method has recently received notable attention.

1.3.2 Preparation of NFs via a one-step method

In the one-step preparation method [63-66], both NP preparation and fabrication of NF are carried out simultaneously in a combined process. Preparation of NF via a one-step method provides some advantages such as minimizing the agglomeration of NPs because in this method the steps of NPs drying, storage, transportation and dispersion of particles in the base liquid media are combined which leads to minimum agglomeration/aggregation/sedimentation of NPs. Nevertheless, scalability of some fabrication methods could be costly and troublesome.

1.4 Stability of NFs

Stability is one of the key features for any NF system in each application, especially heat transfer application. Although a lot of studies have been done about the stability of dispersion containing solid particles [59], fabrication of homogeneous NFs with high stability is still a technical challenge. There is a strong tendency of NPs to form aggregates/agglomeration in the liquid media resulting in not only the clogging of microchannels but also degradation of NF's thermal properties [67]. Therefore, the study of stability of NFs including the key factors which influence the stability as well as the techniques which can be used for the evaluation of the stability of NFs are necessary. In this section we discuss these points.

1.4.1 Factors affecting stability of NFs:

Figure 1.4 shows the factors, which influence the stability of NF and based on that to achieve a stable NF, surface modifiers (such as surfactants), pH adjustment, NF preparation method, mixing/homogenization as well as NPs loading play key role. It should be mentioned that each NF system needs its particular dispersion method to stabilize the NP in base liquid. Sometimes these chemical and physical methods can be combined while in other cases applying one method may be enough to achieve stable suspension.

Solution pH (NP surface charge):

Surface charge on NP's surface is also an important factor for the stability when it is dispersed into a base liquid. Surface charge causes a NP to emit an electric filed resulting in attraction or repulsion of NPs. This charge depends on the pH value of the suspension. It is well known that to
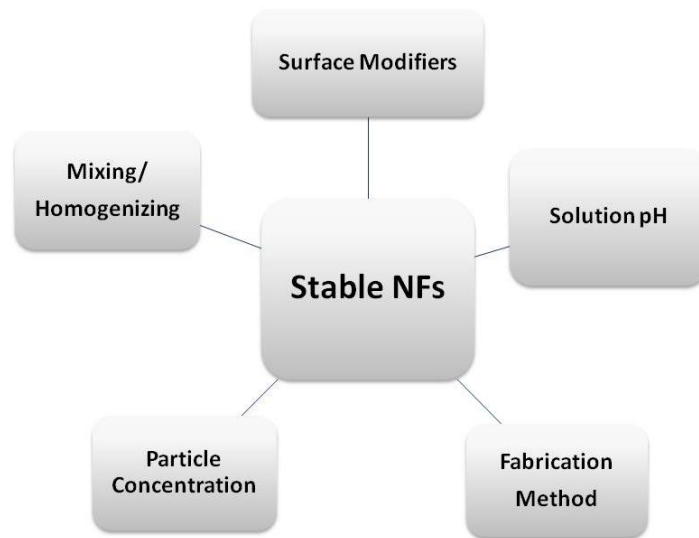
Figure 1.4 Factors affecting stability of NFs

obtain a stable NF, the pH value of the suspension must be far from the Isoelectric Point (IEP) of the particles, where the overall charge on the NPs becomes zero [68-69]. When the pH value of suspension gets close to the IEP, NPs, due to weak repulsive forces between them tend to agglomerate and finally precipitation takes place. If the pH value is adjusted far from the IEP the absolute electrical charge on particles is increased resulting in increasing the repulsive

interaction among NPs. Therefore, by adjusting the pH value of suspension, stability of NF can be well controlled. Optimum value of pH will result in optimal stability for NF system. [70-71]

Surface modifiers:

Surface modifiers are molecules, which applied for modification of surface of suspended particle in the liquid media. Addition of proper surface modifier such as surfactant or other kind of surface modifiers such as polymers or zwitterionic molecules are other ways of avoiding sedimentation of NPs. Surfactants, which comprise hydrophilic head and hydrophobic tails, are typically used to enhance the stability of suspensions. Selection of the surfactant depends on the type of NPs and the base liquid, the NPs surface is modified which result in promising electrostatic repulsion between NPs. By this method hydrophilic surfaces of nanostructured materials (NPs, nanotube, etc) are modified to become hydrophobic and vice versa. It is important to apply adequate surfactant to the suspension to overcome van der Waals attractions [72]. Moreover, depending on the suspension system, selecting the proper surface modifier is most significant part of the procedure. Four types of surfactants including anionic, cationic, nonionic or zwitterionic, or other type of surface modifier such as polymers can be added to the suspensions to improve their stability. So far uses of several surface modifiers have been reported in the literature [67]. SDBS [73-74], Rokanol K7 and Rokanol K3 [75], dodecyl-benzenesulfonic acid (DBSA) [76], dodecyl carboxyl betaine ($C_{12}BE$) [77], sodium hexametaphosphate [78], cetyltrimethylammoniumbromide (CTAB) [79-81], Gum Arabic [82-83], Triton X100 [84], Sodium dodecylsulfate (SDS) [85], some acids such as myristic (tetradecanoic) acid, lauric (dodecanoic) acid [86] and oleic acid [87]; salts such as sodium oleate (NaO) [88], and polyvinylpyrrolidone (PVP) [89-90]. Some restrictions such as temperature range must be taken into account where using NFs at higher temperature may lead to damage the bonding between NPs and surface modifiers [67, 91].

Fabrication method:

Preparation method can also affect the stability of NFs. As mentioned before, two main methods, two-step and one-step, are mainly utilized to fabricate NFs. Since in one-step method, NP manufacturing and NF fabrication are carried out simultaneously, the stages including drying, storage, transportation and dispersion of NP are avoided. It leads to preparation of NF with minimum amount of NPs agglomeration, which finally may result in increasing the stability of

NFs. Therefore, one-step preparation method could show a higher stability for NFs rather than two-step method which may affect the property of NFs positively. There are some studies in the literature reporting the importance of preparation method in better dispersion of NFs [59,67,92]

Concentration of NP:

There is strong tendency among NPs to form agglomerations in liquid media, especially if the solution is very concentrated. Therefore, it is important to control the concentration of NPs in the NF for a better stability. In cases where a high concentration of NPs are required then the use of dispersants, pH adjustment or various mixing methods might be crucial to utilize [93].

Mixing methods:

Using mixing is another method for well dispersing the nanostructured materials in the base liquid media. Up to now different mixing methods including ultrasonic bath, homogenizer and processor have been utilized by different researchers to achieve well-dispersed suspensions [67, 94]. These are energetically powerful instruments to break down the NP agglomerates. Recently many researchers started to utilize a more general accessible apparatus, which is the ultrasonic disruptor [67]. All the mentioned vibration methods will help to obtain a stable NF.

1.4.2 Common tools/techniques to evaluate the stability of NFs

There are some tools/techniques, which are used to assess the stability of suspensions. Figure 1.5 indicates the commonly used tools/techniques to evaluate the stability of suspensions. Zeta potential analysis is the most commonly used technique to evaluate the stability of NFs. By using this technique the optimum value of pH for stabilizing nanostructured materials in the base liquid is identified. This technique displays the potential difference between the layer of liquid attached to the suspended particle and surface of the solid particles. The significance of zeta potential is that its value can be related to the stability of the dispersions. By applying zeta potential analysis, surface charge of the suspended particles in the base liquid will be increased. Therefore, repulsion force between NPs will also be increased resulting in stable suspensions [95]. It should be noted that, normally, when the zeta potential value is less than -30 mV or more than +30 mV, there are strong repulsion forces among NPs, and these kinds of dispersions are believed to have good stability [67, 96-98]. For the suspensions with more than 60 mV (or less than -60 mV), the stability is excellent [67, 99]. There are other methods and tools to evaluate the stability of

suspension, which work based on estimation of rate of sedimentation in dispersions. These methods are: sediment photography, Ultraviolet–visible (UV–vis) spectrophotometry and the sedimentation balance method. Sediment photography [100] is the simplest method to evaluate the stability of suspension. By using this tool, the pictures of settling NPs are recorded and compared versus time, which results in observably estimating the shelf-life of the suspensions. This method cannot be a proper choice for stability evaluation of NFs with slow sedimentation rate. In the UV–vis spectrophotometer [101], light is passed through the suspension then a graph
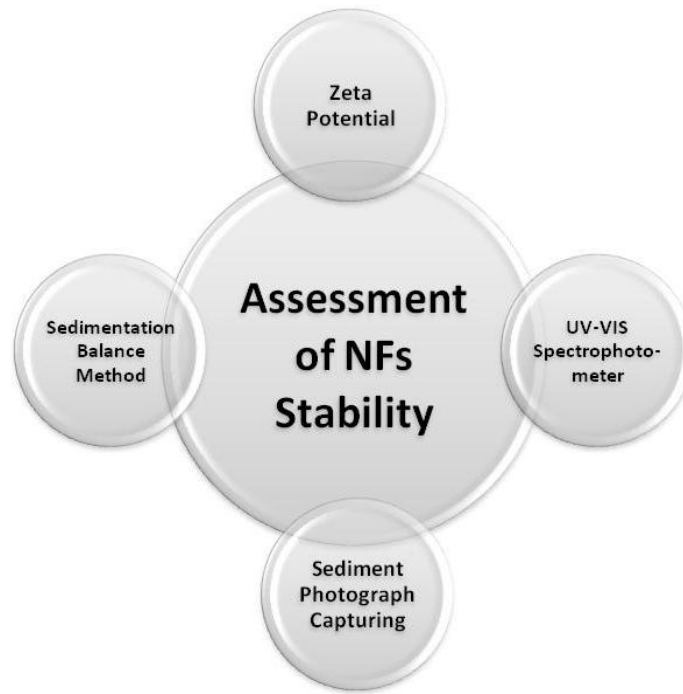
Figure 1.5 Common techniques used for evaluating the stability of NFs

of absorbance against wavelength provides the absorption spectrum of sample. Since it is very difficult for the light to pass through the NFs with high NPs loading, the (UV-vis) method cannot be applied for the NFs with high concentration. In the sedimentation balance method [102] the rate of change of NPs sediment on a tray immersed into a suspension is recorded. As this method is simple, does not have the other methods' limitations as well as it is cheap, it can be a reasonable choice to use for stability evaluation of any NFs systems.

1.5 Thermo-physical and transport properties of NFs

In order to assess the efficiency of a NF for heat transfer applications, one has to evaluate the thermo-physical properties of NF including TC, viscosity, density, specific heat as well as the

flow regime of the fluid. NFs systems are complex suspension and their thermo-physical and transport properties including TC, viscosity and HTC can be influenced by several factors. Figure 1.6 indicates the factors, which affect the NF properties. A very brief overview is presented about the impact of these parameters (figure 1.6) on TC and viscosity of NFs. In this study our aim and focus are to evaluate the TC and viscosity of NFs (as thermo-physical properties) as well as the heat transfer coefficient (HTC) of a selected NF in the laminar flow regime as the transport property of suspension.

1.5.1 Thermal Conductivity (TC) of NFs:

TC is the most significant thermo-physical property of NFs, which must be studied in order to demonstrate the capability of these new engineered suspensions for heat transfer applications.

Figure 1.6 Important parameters/factors, which can influence the NF's thermo-physical properties

This property influences the Nusselt and Prandtl numbers; both present the heat transfer characteristics of a flowing flow. Higher TC is desired for effective NFs for heat transfer applications. The impacts of different parameters on TC of NFs are reviewed based on the reports in the literature.

Effect of pH:

There are few reports on the role of pH on TC of NFs. Xie et al [103] and Lee et al [104] studied water based Al_2O_3 and CuO NFs, respectively and the results showed that TC enhancement is increased with decrease of pH of the dispersions. Yoo et al [105] investigated on Al_2O_3 NFs and showed that TC of NF is enhanced by controlling the pH. Their observation showed that the TC of NFs was improved by controlling pH value so that the maximum TC enhancement was obtained for NFs at pH= 10.94. A study by Karthik et al [106] on water based CuO NFs, with respect to the isoelectric point (IEP), showed that the TC enhancement increases as pH increases and reaches the maximum value close to IEP (at pH ~9), then decreases as pH further increases from 10 to 14. This is contradictory to what would be expected from stability point of view, however a critical agglomerate size could have caused this improvement around IEP. As the materials characterization is rather limited in this paper it is rather difficult to understand the real effect.

Effect of surface modifiers:

Additives such as surface modifiers are used in NF system in order to avoid agglomeration of NPs in the liquid media and based on the NFs system, a proper surface modifier must be chosen. However, although addition of surfactant can avoid the NPs agglomeration, the thermo-physical properties of NFs may be affected by addition of surface modifiers. Depending on the type of additive, its concentration and type of NF application, the impact of additives is different. Nevertheless, most of the researchers have reported that using appropriate surface modifiers with proper amount of them resulted in enhancing the TC of NFs [107]. Investigation by Drzazga et al [108] revealed that using nonionic surfactant for water based Cu (II) oxide NFs has no effect on TC enhancement of NFs. Wusiman et al [109] fabricated water based MWCNTs NFs using SDBS and SDS as surfactants. The results showed that TC of NF decreases with increase of concentration of both surfactants. Sometimes the surface of the nanostructured material is modified by functionalizing them with the proper components to improve their dispersion property. These functional groups also can have effect on TC of NFs. For instance graphene was functionalized by potassium carboxylate and the results revealed that the TC of NFs is related to the functional groups [110].

Effect of temperature:

According to the systematic investigations in the literature the general trends show that the TC is improved by temperature increase [111] except a study done by Masuda et al [112] where they studied on water based NFs containing Al_2O_3, TiO_2 and SiO_2 NPs and observed inconsistent trend; TC enhancement is decreased by increasing the temperature. The TC enhancement also depends on the temperature of system in which NFs are employed. For instance, a study on water based NFs containing TiO_2 NPs (1wt%-35wt%) showed that at higher temperatures, the impact of increasing TC is more than that lower temperature [113].

Effect of base liquid*:*

There are very few publications in the literature about the base liquid effect on TC and viscosity of NFs. Therefore, the impact of base liquid on TC of NFs is not well-understood yet. A general trend can be concluded based on the prior results reported by Moosavi et al [114], Xie et al [115] and Timofeeva et al [116] which exhibited that the TC enhancement for the NFs with low TC base liquids is more than that with higher TC.

Effect of NPs morphology:

Based on the literature the morphology of particle including the size and shape can affect the TC of NFs. The number of publications about the impact of particle size on TC of NFs is limited and there is inconsistency in the reported results. Some investigation show that TC enhancement of NFs is improved when smaller NPs is used while there is another report in the literature showing TC enhancement is increased by increase in particle sizes. Teng et al [117] investigated on particle size effect on TC of NF by fabricating water based Al_2O_3 suspension (with NP size of 20, 50 and 100 nm) and showed that smaller particle size resulted in enhanced TC of NFs. Other study by Chopkar et al [118] also showed that for the water and EG based NFs with Al_2Cu and Ag_2Al NPs, the TC enhancement increases by decreasing the size of NPs. On the other hand, Wang et al [119] studied the effect of CuO particle size on TC enhancement in a water media and observed that the TC enhancement is improved by increasing the particle size. NPs may agglomerate in the base liquid media if the dispersion of NPs is not well. The agglomerates also can influence the TC of NF. Based on the literature they can affect the TC positively and result in higher TC values. For instance a research on water based Al_2O_3 NFs [120] exhibited that high aggregation will result in larger enhancement in TC of NFs while Wu et al [121] investigated on

role of aggregation on TC of NF and observed that the TC was not affected by NPs aggregation even at higher concentration of SiO_2 NPs.

The geometric shape of particle can also influence the TC of NFs. Spherical and cylindrical (nanotube or nanorod) are the two different shapes of particle, whose role in NFs' TC have been reported in the literature. According to those reports, the TC enhancement for cylindrical shape is more than that of spherical particles [111, 122]. Murshed et al [123] fabricated water based TiO_2 particles with spherical and rod shapes and studied the TC of NFs. The results revealed that NFs containing nano-rod shape particles showed TC enhancement over the spherical NPs. The same attempt was carried out by dispersing SiC particles (sphere and cylinder) in water and also EG as base liquids [122]. Results also showed that TC enhancement is higher for cylindrical particles compared to the spheres. Other study by Elias et al [124] also showed that among the different shape of alumina particles (bricks, platelets, blades and cylindrical), the cylindrical shape exhibited the best thermal performance. Jeong et al [125] observed that the TC of ZnO NF with rectangular shape NPs is higher than the one with spherical NPs.

Effect of NP composition:

As mentioned in section 1.2 so far, several compositions such as metallic particles, oxides, ceramic or other type of nanostructured materials have been used in order to fabricate NFs via two-step or one-step methods. As a conclusion in this part it can be mentioned that all the NPs or nanostructures materials could enhance the TC of NF over their base liquid from small enhancement to very high values [111,126]

Effect of NPs concentration:

The TC of NFs is strongly affected by the loading of NPs. There are a lot of studies in the literature reporting about TC enhancements of NFs for different particle compositions. For the same particle composition but at various particles loading, the general trend shows that: the TC enhancement of NFs is increased when the NP loading is increased. This trend has been observed for NFs systems with different base liquids such as water, EG, W/EG mixture and different particle compositions [111,126].

Effect of NF fabrication and NP dispersion method:

The NF preparation method and the techniques for dispersing NP in the base liquid can influence stability and therefore the TC of NF. In the two step method, choosing optimal dispersion method can affect the TC enhancement of NFs. Nasiri et al [127] dispersed CNT in water via two dispersion methods to study their effect on TC of NF. The methods were dispersing CNT with one surface modifier (SDS) but with different ultrasonication (probe and bath) source. Their results showed that the using bath ultrasonication resulted in better stability and higher TC of NFs. Other attempt done by Gahdimi et al [128] by preparing water based TiO_2 NF using SDS surfactant and different ultrasonic processing (bath and horn). Their results showed that highest TC was observed by applying ultrasonic bath in presence of SDS.

Effect of stability of NFs:

The TC of NFs is directly dependent on the stability of NFs so that good stability of NFs leads to grater TC [129]. For instance an investigation by Yang and Du [130] on water based NFs with TiN NPs showed that TC of NFs is directly influenced by the stability of suspensions and they also observed that good stability leads to higher TC of NFs.

Effect of particle crystal structure:

There are some materials, which exist in several crystalline forms. For instance SiC particle exists in around 250 crystal structure forms with two major crystal structures of α and β [131]. Other example can be Al_2O_3 particles which exists in several crystal phases, namely δ- , γ-, θ- , η- and χ- Al_2O_3 [132]. So far there is no result in the literature reporting about the effect of crystal structure on TC of NF. We have investigated on the role of SiC crystal structure on TC of NF and our results have been presented in the result and discussion part of this study [133].

Prediction of the TC of NF:

Although there are several methods for measuring TC of NFs such as Transient Hot Wire method (THW) [134], Transient Plane Source (TPS) [135], temperature oscillation technique [136] and optical methods [137], the two first methods have received most attention. The TC of the NF is calculated from the following formula:

$$k = \left[\frac{q}{4\pi(T2-T1)}\right] \ln\left(\frac{t2}{t1}\right) \tag{1}$$

Where k is the TC of the suspension, q is the constant heat rate (applied electric power), T_1 and T_2 are the temperature at time t_1 and t_2, respectively. The THW firstly was introduced by De Groot et al [138] and then was developed and improved by Nagasaka and Nagashima [139]. The experimental setup comprises a thin Pt wire, which is immersed in the NF. The Pt wire works as an electrical resistance thermometer as well as the heat source. To measure the TC a constant current is passed through the NF and then the rise of temperature of the platinum wire is recorded as a function of time. In the TPS method the element plays two roles of heater and temperature sensor. The use of this method has some advantages. For instance it measures fast in a wide TC range. In this study both TPS and THW were used to measure the TC of NFs.

In order to compare the TC experimental results with the estimated values, using desired model is essential. At the moment there is no model or correlation, which can predict the TC of NFs suitably and precisely. There are different models and correlations in the literature, which have been used to predict the TC of NFs. Some conventional models/correlations are: Maxwell model [140], Hamilton- Crosser model [141], Davis [142] model and Jeffrey model [143].

Maxwell Correlation:

This correlation was introduced for predicting the TC of suspension containing solid particles [140]. The TC is estimated form the equation (2):

$$\frac{K_{nf}}{K_{bl}} = 1 + \frac{3(\alpha-1)\emptyset}{(\alpha+2)-(\alpha-1)\emptyset} \qquad (2)$$

where α is K_p/K_{bl} and K_{bl}, K_p, and K_{nf} are the TC of the base liquid, NPs, and the NF, respectively, and Ø is the volume fraction of the particles. This correlation is appropriate only for the spherical particles and as it can be seen from the correlation it only takes into account the NP concentration and the TC of NP and base liquid. On the other hand Maxwell correlation does not consider other possible factors such as NPs morphology (size and shape), thermal interface resistance between the liquid and NPs, Brownian motion and temperature effects, in prediction of TC of NFs. There are other models or correlation using for predicting TC of suspensions with solid particles considering possible factors which may affect the TC suspensions. Hamilton-Crosser model [141], Davis model [142] and Jeffrey Model [143], are some examples. For instance Hamilton-Crosser model is a proper choice when the shape of solid particle is

considered as a possible factor for the TC of suspension (not only spheres but also other shapes). These models underestimate the TC of NFs and recently new attempts have been done to propose advanced models which can predict well the TC of NFs. In this work and based on the NF systems discussed in the thesis, Maxwell correlation was used to estimate the TC of relevant NFs. Recently new attempts have been done to propose advanced models for the NFs containing particular nanostructured materials such as CNTs to predict their TC. For instance, Xue [144] proposed a model for estimating the TC of NF with CNT as shown in equation (3):

$$9(1-f)\frac{K_e - K_m}{2K_e - K_m} + f\left[\frac{K_e - K^c_{33}}{K_e + 0.14\frac{d}{L}(K^c_{33} - K_e)} + 4\frac{K_e - K^c_{11}}{2K_e + 0.5(K^c_{11} - K_e)}\right] = 0$$

(3)

Where

$$K^c_{11} = \frac{K_c}{1 + (2 * R_k * K_c / d)}, K^c_{33} = \frac{K_c}{1 + (2 * R_k * K_c / L)};$$

(4)

We have used this model to predict the TC of relevant NF and the results have been published in appended paper 3.

1.5.2 Viscosity of NFs:

It is important to explain that achieving a high relative TC value only is not sufficient for utilizing a NF as efficient heat transfer fluid (for cooling applications). In order to select the efficient NF with optimal characteristics for cooling applications, not only TC but also viscosity must be assessed. Viscosity plays an important role in all thermal applications involving flowing fluids and it is defined by internal resistance of a fluid to flow [145]. After addition of NPs to the base liquid, the viscosity of NFs is expected to be greater than their base liquids; however this increase creates a negative effect on the pumping power and heat transfer coefficient (HTC). These are very significant parameters in realistic heat transfer applications. For example, for the laminar flow regime, the pressure drop is directly proportional to the viscosity. Furthermore, Reynolds and Prandtl numbers are affected by viscosity of the fluids and HTC is a function of these numbers. As a result, viscosity is as essential as TC in all engineering systems involving fluid flow [146]. Therefore, the minimal impact of NPs addition in the base liquid is preferred for NFs in cooling applications. Hence, the effects and role of different factors on viscosity of NFs

must be studied and discussed. In the following section the parameters which may affect the viscosity of NFs are briefly reviewed.

Surface modifiers:

There are very few studies in the literature showing the effect of surface modifiers on viscosity of NFs [126]. Depending on the type of surface modifier and its concentration, the viscosity of NFs can be influenced by the surface modifiers. An investigation on water based Fe_3O_4 [147] NFs revealed that the NFs' viscosity is increased by increase of the concentration of the surfactant. Drzazga et al studied the effect of nonionic surfactant on water based Cu (II) oxide NFs. Their result showed that addition of surfactant increases the viscosity of NFs [148].

Effect of NP concentration on viscosity:

There are a lot of reports in the literature on the impact of NP concentration on viscosity of NFs. These investigations have proven the fact that the viscosity of NF increases as the NP concentration increases. It should be mentioned that some research have shown that viscosity increases non-linearly with the increase of NP loading while some other researchers reported that viscosity increase is linear [146].

Impact of NP morphology on viscosity:

There are few studies in the literature reporting the effect of particle morphology including NP size and shape on viscosity of NF. The viscosity of NFs can be influenced by the size of NP. Particle size determines the ratio of surface to volume and in the constant NP concentration, the suspension with smaller particle size has larger solid/liquid interface area which results in increase of NF viscosity [149]. Investigations on dispersion with the same type of NPs and NP concentration but with different sizes (Al_2O_3 NPs in water and EG) revealed that the viscosity of suspension decreases when the size of NP increases [150]. The same trend was observed by Timofeeva et al for the SiC NPs in water media [151]. However, there is contradiction about the size effect on viscosity of NFs. Some studies in the literature report the inverse trend. It means the increase of NF viscosity with increase of NP size. For instance a study on TiO_2 NFs [152] with water as base liquid and different TiO_2 NPs size showed that the viscosity of NF is increased with increase of NP (agglomerate) size. Other contradict result been reported by

Prasher et al [153] where they studied the Al_2O_3 NFs with different NP sizes and propylene glycol as base liquid. Their results revealed that the viscosity of NF is not a function of NP size. About the effect of NP shape on viscosity of NF, there are very few investigations in the literature. These few studies have shown the strong effect of NP shape on viscosity of NFs [146]. For instance Timofeeva et al [154] studied on W/EG based NFs containing Al_2O_3 particles with different shape of platelets, blades, cylinders, bricks and spheres. Their results showed that at the same particle loading non-spherical NPs have higher viscosity compared to the spheres. Moreover, they observed that among all the NFs with different NP shape, the NFs with platelets NPs showed the highest viscosity value. Even the agglomerates can affect the viscosity of NF [146]. NPs can be dispersed well or produce agglomeration in the base liquid media which can affect the viscosity of NFs by providing more increase in that. Recently, a study by Jeong et al [125] showed that viscosity ZnO NF with rectangular shape exhibit more increase compared to spherical NPs.

Effect of temperature on viscosity:

There are numerous studies in the literature discussing about the impact of temperature on viscosity of suspension containing solid particles. Several NFs systems with different base liquids and various materials have been used to study the influence of temperature on NFs viscosity. Most of them have reached to this general trend: viscosity of NF decreases as the temperature increases [126,146] Except, some different research groups have shown inconsistent results where their studies exhibited that the viscosity or relative viscosity of NF is not dependent of temperature [146,153,155].

NP type/composition:

About the effect of NP composition or type of nanomaterial there is also contradictory results in the literature. Wang et al [119] observed that Al_2O_3 NF with EG and water base liquids shows the same value for increase in viscosity while other group [156] reported different values for the viscosity for the same two NF systems. Timofeeva et al [154] also reported that NF viscosity has weak relation with the NP composition (material type) while it has strong dependency with the base liquid.

The role of pH on viscosity:

Viscosity of NFs is also dependent to the pH value of suspensions. As already mentioned the magnitude of pH establishes the surface charge of NP (zeta potential). Existence of repulsion forces between the NP with the same charge will result in minimal interactions among the NP which can affect the viscosity of NF [157]. During the research done by Timofeeva et al [154] the viscosity of Al_2O_3 NF was successfully reduced to 31% while no negative impact on that NF was observed. Jia-Fei et al [157] studied on water based SiO_2 NFs fabricated using NPs with different size in the range from 7 to 40 nm at the pH range from 2 to 7. The results show that for the NFs with NPs more than 20 nm the viscosity is not a function of pH while for the NPs less than 20 nm the viscosity strongly depends on the values of pH. Especially, in the pH range between 5 and 7 the viscosity shows significant fluctuation.

Impact of preparation method:

Fabrication method of NF can also have effect on viscosity of NFs. In one-step method due to the direct forming of NP inside of the base liquid, agglomeration of NP can be minimized which result in minimal impact of NP addition on the viscosity of NF. In the two-step method during the synthesis of NPs, drying, transport and storage process, forming agglomerates is unavoidable; therefore, the viscosity of the NF can be raised. [62]

Effect of particle crystal structure:

As already mentioned, some materials such as Al_2O_3 and SiC have different crystal structures which can affect the thermo-physical properties of NFs such as TC and viscosity. Our findings about the role of crystal structures of SiC particles on viscosity of NFs will be discussed in chapter 3 of this work [133].

Prediction of the viscosity of NF:

Up to now although several models/correlations have been developed to predict the viscosity of suspensions/NFs, none of them is able to estimate the viscosity value satisfactory. Most of these correlations have been derived from Einstein equation [158] who suggested the following formula for predicting viscosity of suspensions containing solid particles:

$$\mu_{nf} = \mu_{bl}(1 + 2.5\emptyset) \tag{5}$$

Where, μ_{nf} is the viscosity of suspension, μ_{bf} is the viscosity of base liquid and $\emptyset$ is the volume fraction of solid particles dispersed in the base liquid. This equation is applied where particle volume fraction is very low, the suspension is dilute and particle has spherical shape. There are several predictive equations or models which can be used to estimate the viscosity of suspension such as Brinkman [159], Batchelor [160], Lundgren [161], Frankel and Acrivos [162]. In this work and according to our NF systems we have applied Einstein equation and the modified Kriger and Dougherty correlation [163] to predict the viscosity of NFs. Kriger and Dougherty correlation was developed in 1959 for estimating the viscosity of the suspensions containing suspended solid particles as shown in equation (6)

$$\mu_{nf} = \mu_{bl}(1 - \frac{\emptyset_a}{\emptyset_m})^{-\eta\emptyset_m} \tag{6}$$

wherein $\emptyset_a$ was proposed by Chen et al [164] as given in equation (7):

$$\emptyset_a = \emptyset(\frac{r_a}{r_p})^{3-D} \tag{7}$$

wherein μ_{bl} and μ_{nf} are the viscosities for the base liquid and the NF, respectively, $\emptyset$ is the volume fraction of the NPs, r_a is effective aggregate size of the NPs in liquid media. It is estimated by DLS. r_p is the primary size of NPs and its value is estimated by SEM. η is the intrinsic viscosity which has a typical value of 2.5 and $\emptyset_m$ is the maximum particle packing fraction which is 0.605 [165]. D is the fractal index and its value is typically 1.8 for NFs [166]. $\emptyset_a$ is the effective volume fraction of aggregates.

1.5.3 Heat Transfer Coefficient (HTC) of NFs:

It must be mentioned that, TC is not the only factor defining the heat transfer efficiency in the NFs systems. For instance, in the forced flow systems due to the pumping NFs, the efficiency of the NFs with various NP and base liquid systems are dependent to the fluid properties (such as TC and viscosity) and also the flow regime (laminar or turbulent modes). The increase in TC of NFs favors the HTC while it does not get any benefit from the increase in viscosity of NFs. Therefore, NFs with higher TC and minimal impact of introduction of NPs to the base liquid will be beneficial for HTC enhancement of NFs. All parameters which can affect the TC and

viscosity are also able to influence the HTC of NFs. In this thesis we have investigated HTC of a particular NF for the laminar flow regime as will be discussed later.

Prediction of the HTC of NFs in the laminar flow regime:

There are several equations in the literature used for predicting of HTC for the laminar flow regime such as Shah Equation [167], Hausen Equation [168], Stephan Equation [169] and etc. In this work we have used Shah Equation as given in the equation (8) to estimate the HTC of NFs for the laminar flow regime.

$$Nu_x = \begin{cases} 1.302x^{*-\frac{1}{3}} - 1 & x^* \leq 0.00005 \\ 1.302x^{*-\frac{1}{3}} - 0.5 & 0.00005 \leq x^* \leq 0.0015 \\ 4.364 + 8.68(1000x^*)^{-0.506} \exp(-41x^*) & x^* > 0.0015 \end{cases} \tag{8}$$

Where

$$x^* = \frac{x/D_i}{RePr}. \tag{9}$$

and

$$Pr = \frac{\mu\, C_P}{K} \tag{10}$$

Where *D_i, Re, Pr, μ, C_p* and K are diameter, Reynolds number, Prandtl number, viscosity and TC, respectively.

1.6 NFs optimization process in this work

The main focus of this study was preparing efficient NFs with optimal properties for heat transfer applications. Figure 1.7 displays the optimization procedure during our attempts for the formulation of effective NFs, where the focus is on the formulation of NFs with improved TC and minimal viscosity increase, which is expected to yield enhanced HTC of NFs. For this purpose, different NFs systems were designed and evaluated at each stage, where composition, crystal structure, particle morphology and concentration of nanoparticles, along with the base liquid composition has been investigated for NF stability. The optimization process was carried out as long as desired characteristics for NF were obtained in the related stage. For instance, if a NF did not show minimum required stability to perform TC and viscosity tests, it must be sent

back to the optimization step where its stability was improved by the methods discussed in section 1.4. For example suitable surface modifier can be used to optimize the stability of NFs. In any stage regarding the thermo-physical property evaluation; depending on the obtained values for TC and viscosity; the application assessment of NF can be done to find any potential application. For example if one NF system showed higher TC enhancement compared to the
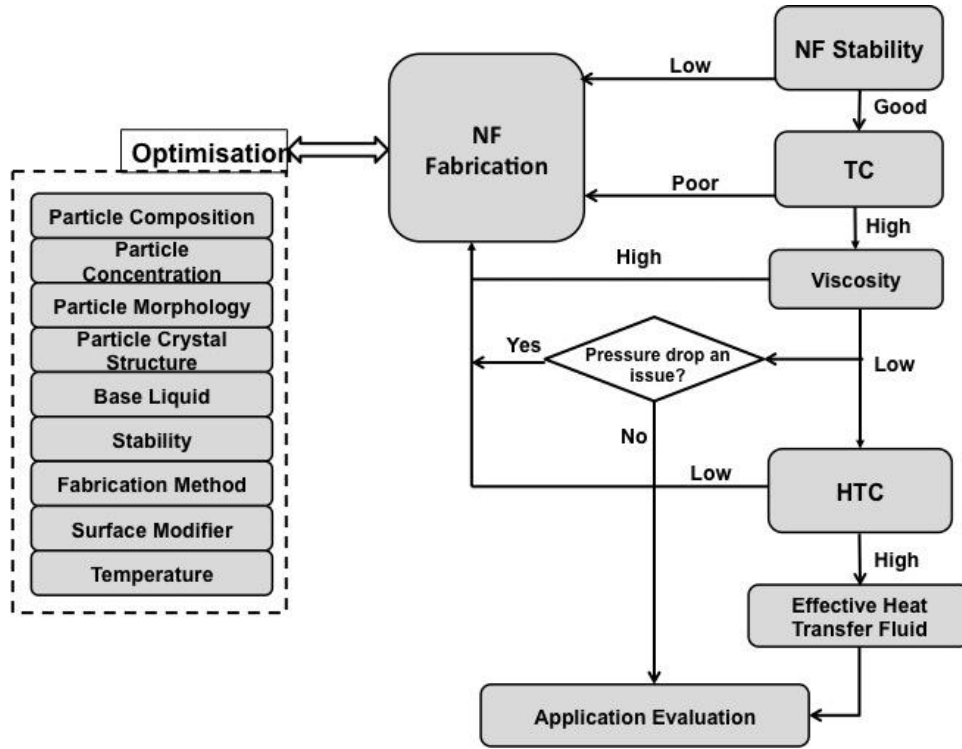

Figure 1.7 Optimization process for the formulation of effective NFs for heat transfer applications

viscosity increased; however, the difference was not sufficient to consider it as a suitable candidate for HTC test, other factor such as pressure drop should be taken into account. If pressure drop is a significant issue in that particular application, the NF must be re-sent to the optimization stage; otherwise it can be evaluated for proper application.

1.7 Objectives of the Thesis

Our final goal is to demonstrate efficient NF formulations, advancing our understanding of the interplay between different material qualities to develop NF for commercial scale heat transfer/exchange applications. In summary, the objectives of this thesis are to study and develop an understanding of NFs thermo-physical properties in detail, focusing on the TC and viscosity, and their dependence on the followings:

- NP composition and concentration

- NFs' stability

- Use of appropriate surface modifiers

- Particle size

- Impact of preparation method

- Base liquid effect

- Role of crystal structure

Based on our findings our ultimate goals are:

- To fabricate NFs with optimal thermo-physical properties which show the highest TC with minimal increase in viscosity

- To develop highly stable NF with the enhanced thermal transport property in order to use in practical heat transfer applications

2. Experimental
2.1 Materials and Methods

Two main preparation methods (two-step and one-step) were used to fabricate/synthesis of the NFs used in this study. For all the NFs systems studied in this work two-step method was used except for DEG based Copper NFs, which was synthesized via one-step method. Figure 2.1 displays the typical procedure for fabrication of NFs using two-step method in this study. Dashed boxes may be used / needed based on the NFs systems (base liquid material and composition of solid particle). The procedures for fabrication of different NFs via two-step method are summarized below: (For all NFs, ultrasonic mixing (Chemical instruments AB, CiAB, Sweden) was used for the dispersions).

For fabrication/synthesis of different NFs required materials, chemicals and reagents were purchased from different suppliers or research centers. The materials for each NF systems are listed below, prior to definition of the NF fabrication method used.

Water based MPSiO$_2$ NFs:

First of all known weights of MPSiO$_2$ particles (purchased from Nanologica AB, Stockholm, Sweden) were dispersed in water; followed by ultrasonicating the dispersion in an ultrasonic mixer for ~15 min. Then the pH value of the suspension was adjusted to 9 by adding 0.5 M NaOH solution. Finally the ultrasonic mixing was performed again for the suspension (15 min). The obtained MPSiO$_2$ NFs were stable for at least a day without visual precipitation. The thermal conductivity and viscosity of NFs were measured within less than 24 h.

DEG based Cu NFs (one-step and two-step methods):

For one-step method synthesis, Polyvinylpyrrolidone (PVP, MW: 10000 g/mol), diethyleneglycol (DEG, C$_4$H$_{10}$O$_3$ ≥99%) copper acetate monohydrate (Cu(ac)$_2$·H$_2$O, MW:199.65 g/mol, ≥99%) as copper source and L-ascorbic acid (C$_6$H$_8$O$_6$, MW:176.12 g/mol, ≥99%) and DEG were obtained from Sigma Aldrich. For the two-step method preparation, Cu NPs and micron size particles (MPs) were purchased from Alfa Aesar, Germany.

DEG based Cu NFs:

A one-step microwave-assisted synthesis procedure (figure 2.2) was used to synthesis/fabricate of Cu NF with DEG as the base liquid. The procedure was adopted from Blosi et al [170] where

molecular weight of PVP was changed from 55000 Da to 10000 Da. For synthesizing the Cu NFs, first of all PVP was dissolved in 10.5 mL of DEG (base liquid) and this solution was heated to 170 ^{o}C for 10 minutes in a microwave oven under magnetic stirring. When the solution reached to synthesis temperature, two DEG solutions were added into the hot PVP solution: 2 mL of Cu(ac)$_2$·H$_2$O-DEG solution and then 3.5 mL of the ascorbic acid-DEG. After adding metal precursor, a green solution was achieved, which turned to dark red when the ascorbic acid solution was added, showing the nucleation of metallic Cu NPs. The one-step Cu NFs obtained by microwave-assisted route was found to be colloidally stable for several weeks, without any visual sedimentation. For fabricating NFs with various concentrations of Cu NP, and because of volume constraints of the MW cavity, several small volume batches of 0.4wt% Cu NF were prepared. Then to keep the sample history and particle size the same, NFs with higher concentrations (0.6, 0.8 and 1.6wt %) were prepared by centrifuging and concentrating these samples.

Two-step Cu NFs and MFs were fabricated by dispersing a known weight of Cu solid particles in DEG as the base liquid. After dispersing the ultrasonic mixing of the suspension was carried out for 25 min and the fabricated NFs/MFs were stable for at least 36 h without any observable precipitation.

CNT NFs:

Multi-walled CNTs, Triton X-100 (TX, 100% pure, nonionic) and Gum Arabic (GA, 100% pure) were received from the Research Institute of Petroleum Industry (RIPI), Iran.

A series of water based suspensions with as received CNT (AR- CNT) at various concentration (0.025, 0.05 and 0.1 wt%) were dispersed by ultrasonic mixing and followed by the addition of Gum Arabic (GA) and Triton X-100 as surface modifiers. Then further bath sonication was performed to achieve more homogeneous suspension. In order to study the effect of heat treatment on CNT samples, Heat treated CNTs (HT-CNTs) were made by heating the AR-CNTs at 300 °C for 2 hour in air. Then new series of water based NFs were fabricated by dispersing HT-CNTs with the same concentrations of the first series of NFs. To stabilize the HT-CNTs in the water media the same surface modifiers with the same concentrations were added. Also the same preparation method in terms of sonication method and time were applied during NFs
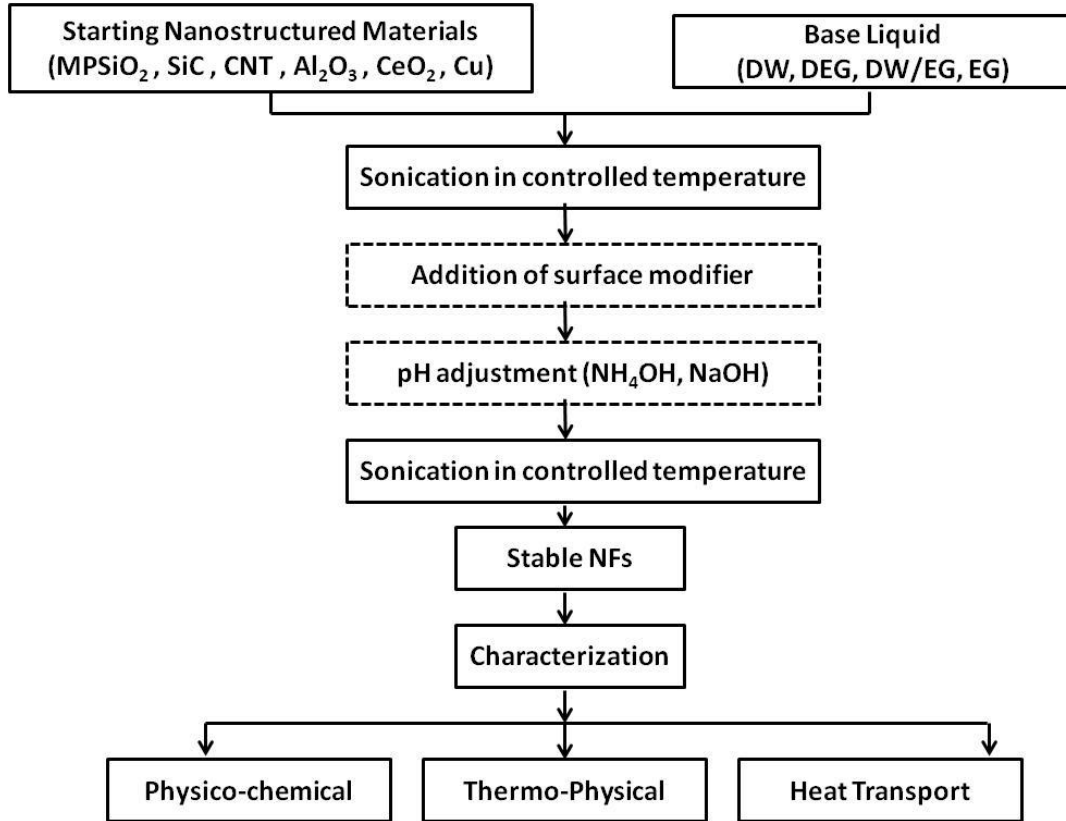
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┌─────────────────────────────────┐        ┌─────────────────────────┐
│   Starting Nanostructured Materials │        │      Base Liquid        │
│ (MPSiO₂ , SiC , CNT , Al₂O₃ , CeO₂ , Cu) │        │  (DW, DEG, DW/EG, EG)   │
└─────────────────────────────────┘        └─────────────────────────┘
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Figure 2.1 flowchart:

- Starting Nanostructured Materials (MPSiO₂, SiC, CNT, Al₂O₃, CeO₂, Cu)
- Base Liquid (DW, DEG, DW/EG, EG)
- Sonication in controlled temperature
- Addition of surface modifier
- pH adjustment (NH₄OH, NaOH)
- Sonication in controlled temperature
- Stable NFs
- Characterization
- Physico-chemical | Thermo-Physical | Heat Transport

Figure 2.1 Typical procedure for fabrication and evaluation of NFs via two-step method in this research

preparation stages. For obtaining optimum dispersion property, the pH of all NFs containing AR-CNT and HT- CNT was adjusted between 9.5 and 10 by adding NaOH solution. The fabricated CNT NFs were stable for more than 6 months.

Clay (I),(II),(III) NFs:

The clay NFs were prepared from two sources. Clay (I, laponite) is synthetic clay with the average density of 2.53 g/cm^3. Clays (II) and (III) are platelet clays (kaolinite, aluminosilicate) with an average density of 3.5 and 4.0 g cm^{-3}, respectively and were purchased from Amberger Kaolinwerke, Germany. Clay (I) and (II) NFs were fabricated by Primary Dispersions Limited, UK, and clay (III) NF were made by ItN Nanovation, Germany, without using surfactant.
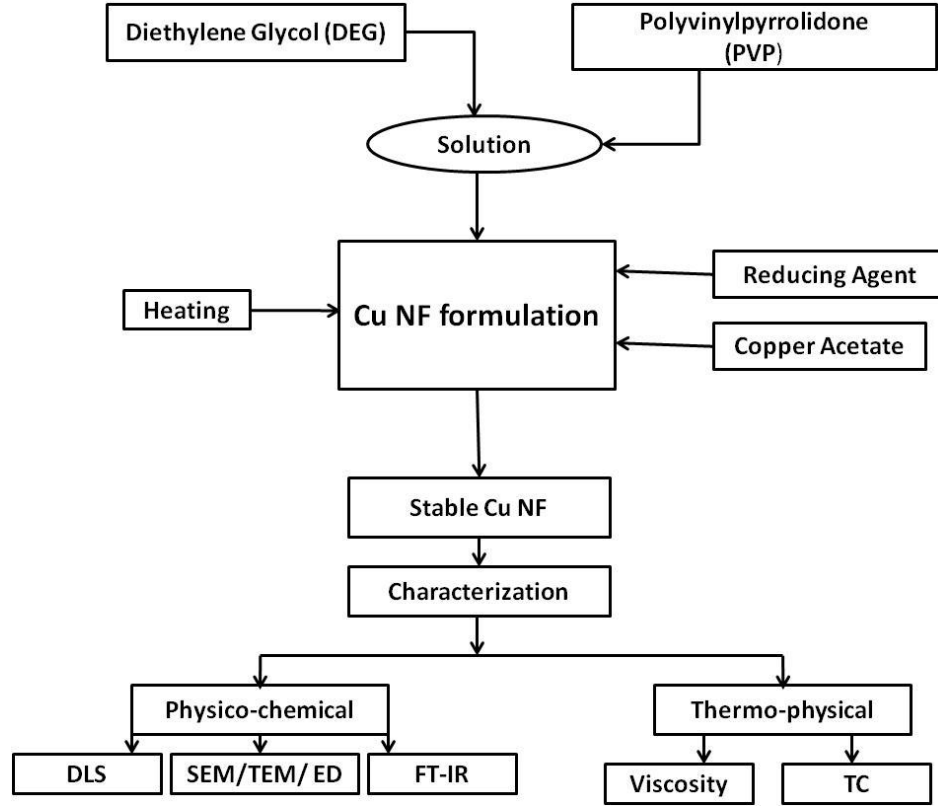
Figure 2.2 One-step method for fabrication of Cu- DEG NFs using microwave-assisted method and its characterization (paper 5)

Al₂O₃ NFs:

Al_2O_3 NPs were prepared by ItN Nanovation, Germany. The source of the NP was Al_2O_3 hydroxyl chloride. To disperse these NPs in water media, they were coated by octyl silane.

CeO₂ NFs:

The CeO_2 NPs were lab-made [171]. EG ($C_2H_6O_2$, 99.8%) was purchased from Sigma Aldrich.

Water and W/EG based α- and β-SiC NFs (paper 6 and 7):

Silicon Carbide (SiC) particles with different crystal structure of beta type (β-SiC) and alpha type (α-SiC) were acquired from different institutes/suppliers including PlasmaChem GmbH (Germany), Superior Graphite (USA) and ENEA (Italy). EG and sodium hydroxide (NaOH) were acquired from Sigma Aldrich and Merck KGaA (Germany), respectively. All the particles were used as received, without any further purification.

A series of W/EG based NFs (9 wt%) were prepared by dispersing a known weight of α-SiC and β-SiC particles in W/EG (50:50 by wt) base liquid using ultrasonic mixing. For this purpose, first the suspension was sonicated for 15 min. Then in order to achieve stable suspensions, the pH value was adjusted around 9.5, by addition of NaOH, followed by sonication of NFs for another 15 min. The NFs with 6 wt% and 3wt% α-SiC NPs were fabricated by diluting the 9wt% NF with proper amount of water and W/EG base liquids.

2.2 Analytical/ Characterization techniques

2.2.1 Physico-Chemical Characterization

2.2.1.1 Morphology/Microstructure Evaluation

Scanning electron microscopy (SEM): SEM analysis was carried out to study the Microstructure and morphology of NPs/nanostructured materials (using FEG-HR Zeiss-Ultra 55 SEM system). For performing SEM analysis for NF samples, around 2 ml of each suspension was dried for around 8 hours at 80 ^{o}C, which were then used for SEM analysis.

Transmission electron microscopy (TEM): TEM analysis of the particles was performed using JEOL 2100 at 200 kV acceleration voltages. The TEM samples were made by dipping a carbon-coated copper grid in a dilute suspension containing solid particles and follow by drying the TEM grid in ambient environment. Ethanol was used as dispersion media.

X-Ray Diffraction analysis (XRD): To identify and study the crystal structure of nanomaterials, X-ray powder diffraction (XRD) was performed on a Philips X´pert pro super Diffractometer with Cu Kα source (λ=1.5418 Å).

2.2.1.2 Surface Functionality Evaluation

To study the surface chemistry of solid particles and solid/liquid samples, Fourier Transform Infrared Spectroscopy (FTIR) was utilized. For this purpose, Nicolet Avatar IR 360 spectrophotometer, in the range between 500 cm^{-1} and 4000 cm^{-1} was applied for the all NF samples and NPs/nanostructured materials used in this study. For the NFs or any liquid samples, one drop of sample was placed on the sample holder while for the solids few mg of sample was used to perform the FT-IR analysis.

2.2.1.3 Particle Size/ Zeta Potential Analysis

Dynamic Light Scattering (DLS) analysis was performed to estimate the average dispersed size of NPs in the base liquid media. For this purpose the Beckmann-Coulter Delsa Nano C system was also utilized to analyze the size of solid particles in liquid media. The samples were prepared using few drops of NFs dispersed in excess base liquid to get a permissible level (detection by instrument showing optimum level) in dilution to get optical transparency, followed by sonication. Zeta potential analysis of NPs/nanostructured materials was done for assessing the NFs stability using Beckmann-Coulter Delsa Nano C system where zeta potential is measured by determining electrophoretic movement of charged particles under electric field. For sample preparation a diluted solution was prepared and sonicated before measurement. The Titration was carried out using 0.1M HNO_3 as acidic and 0.1M NaOH for base range.

2.2.1.4 NFs Stability Evaluation:

The stability of NFs was measured using the sedimentation balance method wherein the weight of NPs in the NF sample, which accumulates on a tray submerged in the suspension, was measured by an accurate scale. In fact the weight of NPs on the submerged tray can be related to the fraction of NPs, which are still dispersed in the NFs. After a period of time, the sedimentation

Figure 2.3 The set-up used for measuring the sedimentation rate of NFs

rate approached zero, where it can be assumed that the NPs remaining in the fluid were actually stably dispersed. It should be mentioned that two factors can be measured using this technique: the sedimentation rate and the time at which no more NPs settled on the platform. In this work

the set up presented in figure 2.3 was used to measure the sedimentation rate of NPs (evaluation of NFs stability). The submerged tray in the samples was indirectly connected to the scale pin. Consequently, the scale could measure the weight of the sedimented NPs on the tray continuously.

2.2.1.5 Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES):

Concentration of Cu in the NFs was determined by using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES, Thermo scientific, iCAP 6000 series)

2.2.1.6 Thermogravimetric Analysis (TGA)

TGA analysis (using TGA-Q500, TA Instruments) was performed to study the influence of heating on as-received carbon nanotube.

2.2.2 Thermo-physical and Transport Property Characterization

2.2.2.1 TC Measurements

Thermal conductivity of NFs was measured and evaluated by using two different techniques including Transient Plane Source (TPS, HotDisk model 2500) and Transient Hot Wire (THW, KD2-Pro- Decagon device). In order to evaluate the accuracy of the instruments, thermal conductivity of DW was measured at 20 ^{o}C and the results were compared to the data produced by International Association for the Properties of water (IAPWS) [172]. The validity test revealed the deviations of $\pm$ 2% and $\pm$ 1% for the TPS and THW techniques, respectively.

2.2.2.2 Viscosity Measurements

Viscosity of NFs was measured and assessed using a coaxial cylinder viscometer (Brookfield model DV-II+ Pro). The Viscosity of DW was measured at 20 ^{o}C and compared to the IAPWS [172] data to validate the accuracy of viscometer. The deviation of $\pm$ 4% was observed.

2.2.3 Heat Transfer Coefficient (HTC) Tests

In order to perform HTC test, a closed-loop system as displayed in Figure 2.4 was utilized to perform the forced convective experiments for the NF. To test the validity of the HTC setup, the local Nusselt numbers of W/EG and DW calculated from experimental data at inlet temperature of X was compared with the predicted values by Shah Correlation [167]. The variations of

experimental data for the particular NF estimated similar to the base liquid, which was within ±15% compared to the Shah Correlation. These results point out that the classical correlation such as Shah Equation can successfully predict the HTC of NF in laminar flow regime.
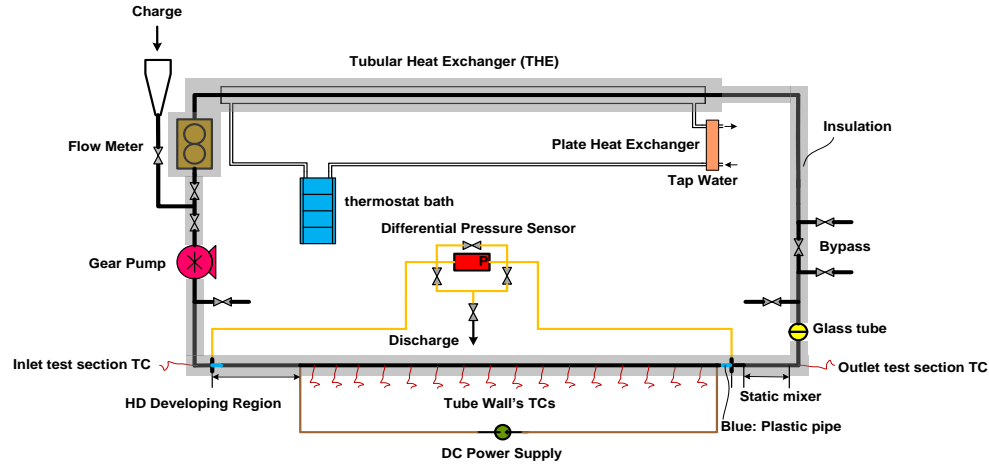

Figure 2.4 Diagram for the HTC experimental set-up [173-174]

3. Result and Discussion

3.1 Stability of NFs; its importance, method for evaluate and enhance the stability of NFs (Appended papers 1, 2 and 3)

Our literature survey and experiences in dealing with different NF systems showed that stability of NFs is a significant factor to consider in their performance evaluation. On the other hand stability is the first property, which must be considered as suspensions containing solid nanostructured materials without good stability cannot be investigated suitably. Therefore, the research work was designed to study the methodologies of assessing and improving stability of NFs as well as the role of stability on thermo-physical properties of NFs. In the first step of this work, mesoporous silica (MPSiO$_2$) particles as a ceramic nanostructured material was selected and dispersed in water media to fabricate MPSiO$_2$ NFs using a two-step method. A mesoporous material is a material, which contains pores with diameters from 2 to 50 nm [175]. We fabricated these novel MPSiO$_2$ NFs system for the first time and characterized them for heat transfer applications. The reason for testing this nanostructured material was due to its higher surface area. In fact at equal amount of material the MPSiO$_2$ NPs provide much more surface area compared to the SiO$_2$ NPs. Therefore, when it is dispersed in the liquid media may enhance the thermo-physical properties of NFs. For this purpose commercial MPSiO$_2$ particle was obtained and characterized using several techniques. The morphology analysis of MPSiO$_2$ particles was performed by SEM and a micrograph is shown in figure 3.1(a). Spherical morphology was observed with the average primary size of 350±100 nm as estimated form SEM.
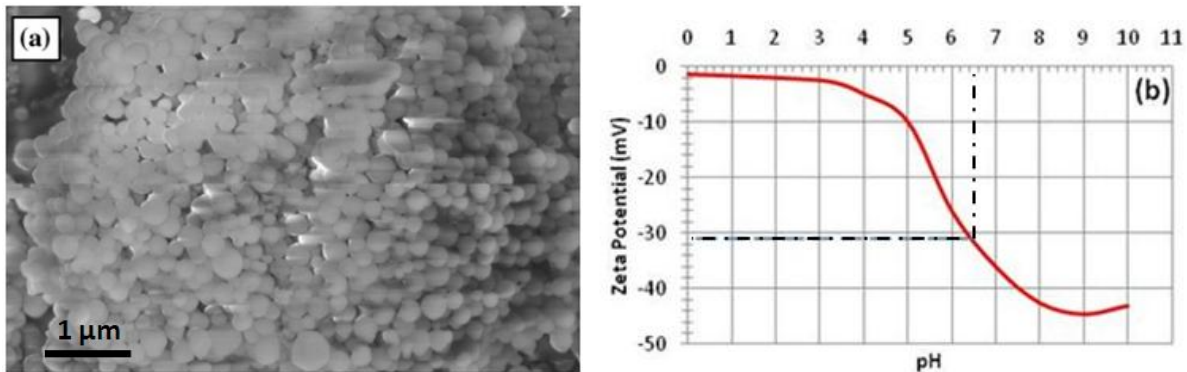

Figure 3.1 (a) SEM image of MPSiO$_2$ particles **(b)** Zeta potential as a function of pH for MPSiO$_2$ particles (paper 1)

In order to assess the stability region of NFs, zeta potential analysis was carried out and the result is displayed in figure 3.1(b). According to zeta potential analysis result the samples could be

stable at the pH values between 6.5 and 9. In order to obtain samples with maximum possible stability the pH value of NFs were set at ~9 where the surface of $MPSiO_2$ particles has maximum charge. Finally, thermo-physical property measurements including TC and viscosity were performed to evaluate the capability of these kinds of NFs for heat transfer applications. For that end, several water based NFs with different concentration of $MPSiO_2$ particle (1, 2,3 and 6 wt%) were fabricated using two-step method. The procedure of NF fabrication has been displayed in figure 2.1 where pH of samples were set at ~9 based on zeta potential analysis results. The NFs were stable for a day and therefore there was enough time to evaluate the TC and viscosity of NFs. The TPS method was utilized to measure the TC of NFs in different temperatures from 20 ^{o}C to 60 ^{o}C. The results are shown in figure 3.2 (a) where all NFs containing $MPSiO_2$ particles
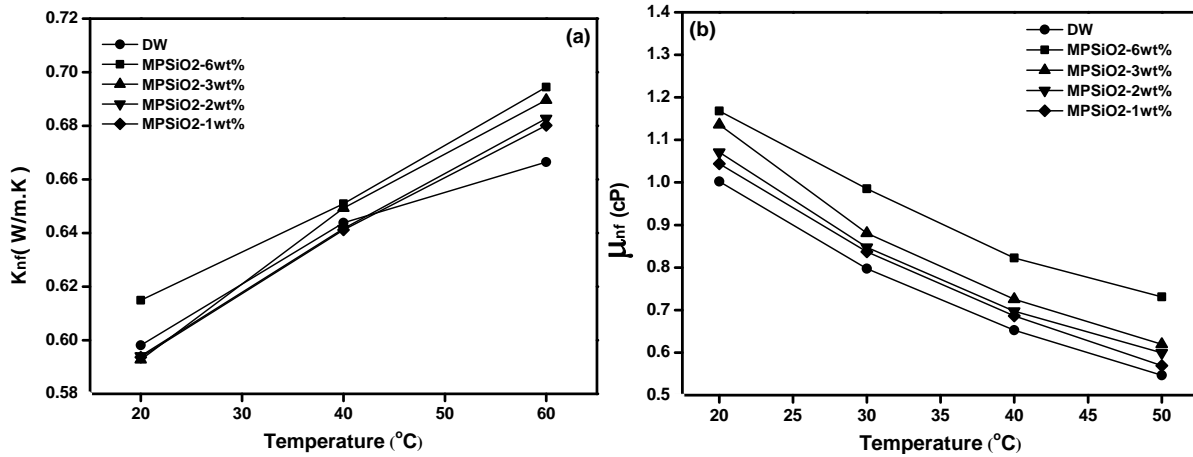

Figure 3.2 (a) TC **(b)** viscosity of NFs with $MPSiO_2$ concentration ranging between 1 and 6 wt% and DW as base liquid at various temperatures (paper 1)

exhibited higher TC values compared to the base liquid. Moreover, it can be seen that TC of $MPSiO_2$ NFs increase as particle concentration as well as temperature increase. The maximum TC enhancement of ~4.1% was obtained for $MPSiO_2$ NF containing 6wt% particle at 60 ^{o}C. The same set of water based NFs with various concentration of $MPSiO_2$ particle were analyzed for their viscosity property at the temperature range from 20 ^{o}C to 50 ^{o}C, and the results are displayed in figure 3.2 (b). The viscosity of $MPSiO_2$ NFs increases as particle concentration increases and decreases with increase of temperature. Increase in viscosity of ~34% was observed for NFs with 6wt% particle loading at 50 ^{o}C. When the obtained values for TC enhancement and increase in viscosity for $MPSiO_2$ NFs are compared, it can be seen that in all cases, TC enhancement is lower than increase in viscosity indicating that, they need to be

optimized for their thermo-physical properties as well as stability issue. On the other hand since the use of surface modifiers was avoided and only pH adjustment was used to stabilize $MPSiO_2$ particles in water media, resulted in poorer stability property (only a day) of the NFs. Therefore, the stability of these NFs must be optimized which may lead to enhance the thermo-physical properties. After our first experience with $MPSiO_2$ NFs, two challenges of enormous difference between TC enhancement as well as poor stability of NFs were recognized. Therefore, in the next stage we focused on developing a method to monitor the stability of NFs as well as improving this significant property of NFs. We planned to use a simple method to evaluate the stability of NFs and study the effect of stability on thermo-physical properties of NFs. For these purposes, several commercial NFs made by two-step method were obtained and their stability were evaluated and monitored by sedimentation balance method. The characteristics of the NFs evaluated in this section are listed in table 3.1. Figure 3.3 (a) shows the sedimentation behavior for three different water based clay NFs, which were measured for around 12,000 minutes (more

Table 3.1 Characteristic of the NFs tested for stability property

Type of NP	Clay (I), (II), (III)	Al_2O_3	CeO_2	CeO_2
Base fluid	DW	DW	EG	W/EG (50% Vol)
Concentration (wt%)	9, 9, 1.75	9	1, 2	9
Density of solid NP (g/cm^3)	2.53, 1.75, 1.75	3.97	7.22	7.22

than 8 days). These graphs exhibit that the total sedimentation of NPs during the 12,000 minutes differs noticeably among the clays. A part of this difference can be related to the difference in density of NPs. However, generally these clay NFs have a tendency to sediment in a short time, particularly clay (III). As the test results revealed, NFs with clay (III) took only 80 minutes to sediment the NPs completely while this time were around 2500 and 1500 minutes for clay (I) and (II) respectively. In order to study the effect of NP concentration on stability of NFs, two EG based CeO_2 NFs with concentrations of 1 and 2wt% were used and evaluated for 3000 minutes. The sedimentation amount is displayed in figure 3.3 (c) wherein both 1 and 2wt% EG based CeO_2 NFs showed an approximately similar sedimentation trend. However, the NF with 2wt% NP concentration exhibited a linear behavior. Figure 3.3 (d) shows the sedimentation rate for CeO_2 NFs where slightly higher rate of sedimentation was observed for NF containing 2wt% NP, most probably due to the higher NP concentration. Moreover, as figure 3.3 (d) shows the rate of sedimentation of NF with 2wt% NP loading approaching nearly constant after a short time,

which reveals the linear behavior of sedimentation for this NF during the investigated time. From both figures related to CeO_2 NFs, it was obviously observed that NF containing more NP loading would have a higher rate of sedimentation. The stability of water based Al_2O_3 NF containing 9wt% NP was evaluated for 25,000 minutes (around 17 days) and the result for sedimentation amount is illustrated in figure 3.3 (e) and as one can see the amount of sediment on the tray varies between 0 to and 1.7 g during the measurement. Figure 3.3 (f) shows the rate of sedimentation for Al_2O_3 NF and based on that the sedimentation rate below 0.0002gr/min was observed. This rate is 10 times lower than the measured results for NFs with clays in figure 3.3 (b). Furthermore, the rate of sedimentation reduces as time increases, which may be due to the reduction in the amount of NP with larger size in the suspension. The figure 3.3 (f) also shows that the rate of sedimentation approaches almost zero after around 20,000 minutes. In the next step the TC of water-based NFs containing clay (I), (II), and (III) with poor stability property and TC of water-based Al_2O_3 (9wt%) NF with good stability was measured at 20°C for every 10 minutes for around 33 hours. The results are presented in figures 3.4 (a) and (b) and based on that the TC enhancement of 5.9%, 7.9% and 4.2% were obtained for NFs with clay (I), (II), and (III) respectively. Nevertheless after nearly 130 minutes for clay (I) NF, 270 minutes for clay (II) NF and 70 minutes for clay (III) NF, the TC values became the constant value of 0.591W/mK (1% lesser than TC of water at 20 $^{\text{o}}$C). These results were in agreement with the obtained results for the sedimentation rate measurements in figure 3.3. Furthermore, the lower value of TC for NF containing clay (III) compared to values for clay (I) and (II) at the first measuring point is because of the lower NPs concentration in this NF. Contrariwise, the TC of Al_2O_3 NF exhibits only a small reduction in TC during the whole experimental time, as shown in figure 3.4 (b). The average value of TC enhancement for Al_2O_3 NF was 11.9% indicating its excellent stability. Other attempt was done to study the effect of stability on viscosity of NFs. For this purpose, the viscosity of CeO_2 (9wt%) in W/EG as a NF with poor stability and a NF with good stability (water-based Al_2O_3 with 9wt% NP loading) were measured every 15 minutes for around 18 hours at three separate shear rates of 14, 45 and 75 rpms at 20 $^{\text{o}}$C. The results are displayed in figure 3.4 (c) and (d) where the CeO_2 NFs exhibited higher viscosity values compared to the viscosity of base liquid; however the values reduced gradually at all rpms. The reason for obtaining dissimilar values in different speeds may be due to non-Newtonian behavior of these NFs.
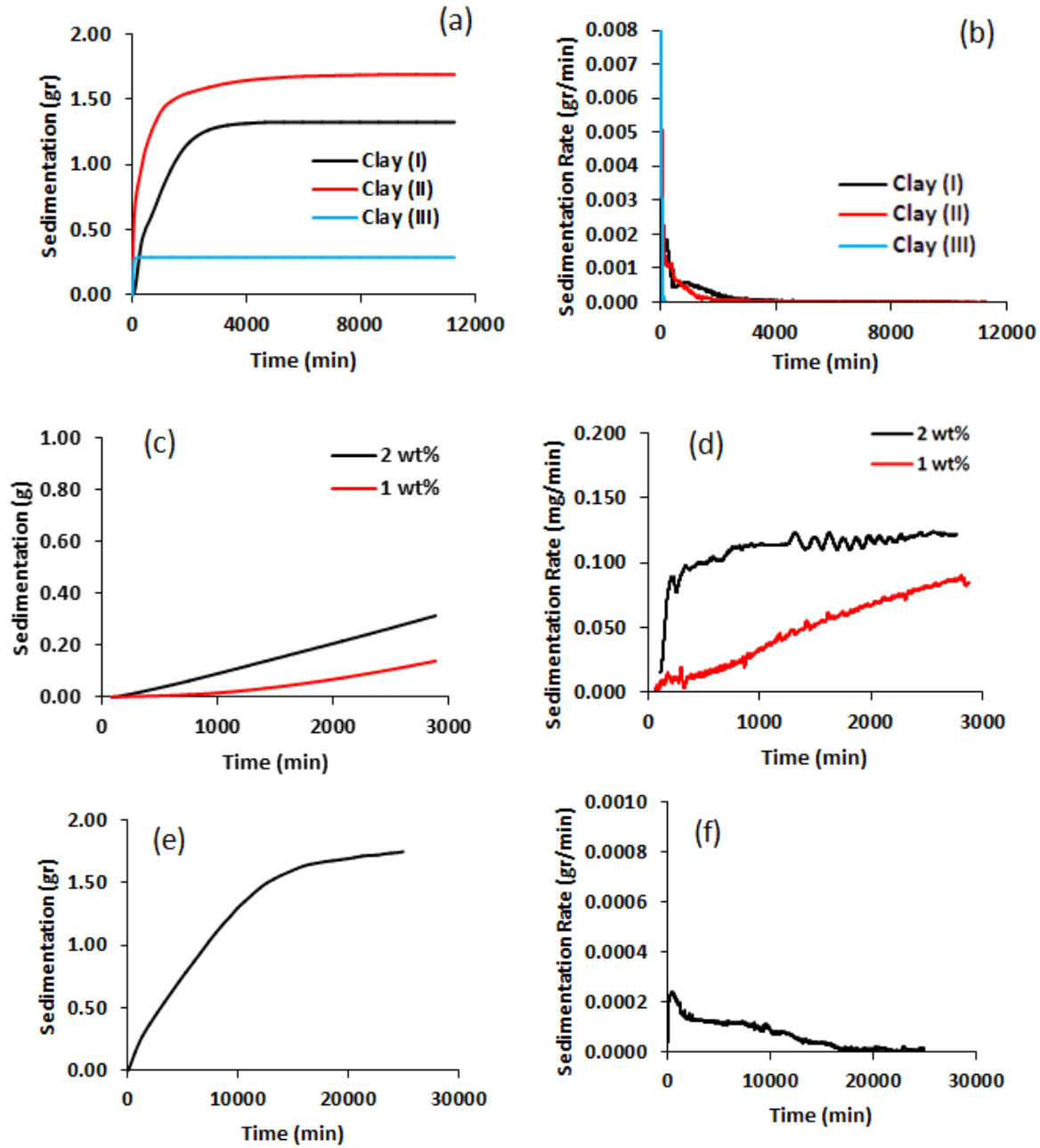
Figure 3.3 Sedimentation amount and sedimentation rate for NFs containing **(a)** and **(b)** clays (I), (II) and (III); **(c)** and **(d)** CeO_2 NPs (1 and 2 wt%) in EG ; **(e)** and **(f)** Al_2O_3 NPs (paper 2)

As the sedimentation of NPs is time dependent and its amount is different for each rpm; thus, determination of exact value for the viscosity of CeO_2 NFs is impossible. On the contrary for Al_2O_3 NF, the values for viscosity are almost uniform and time independent during the
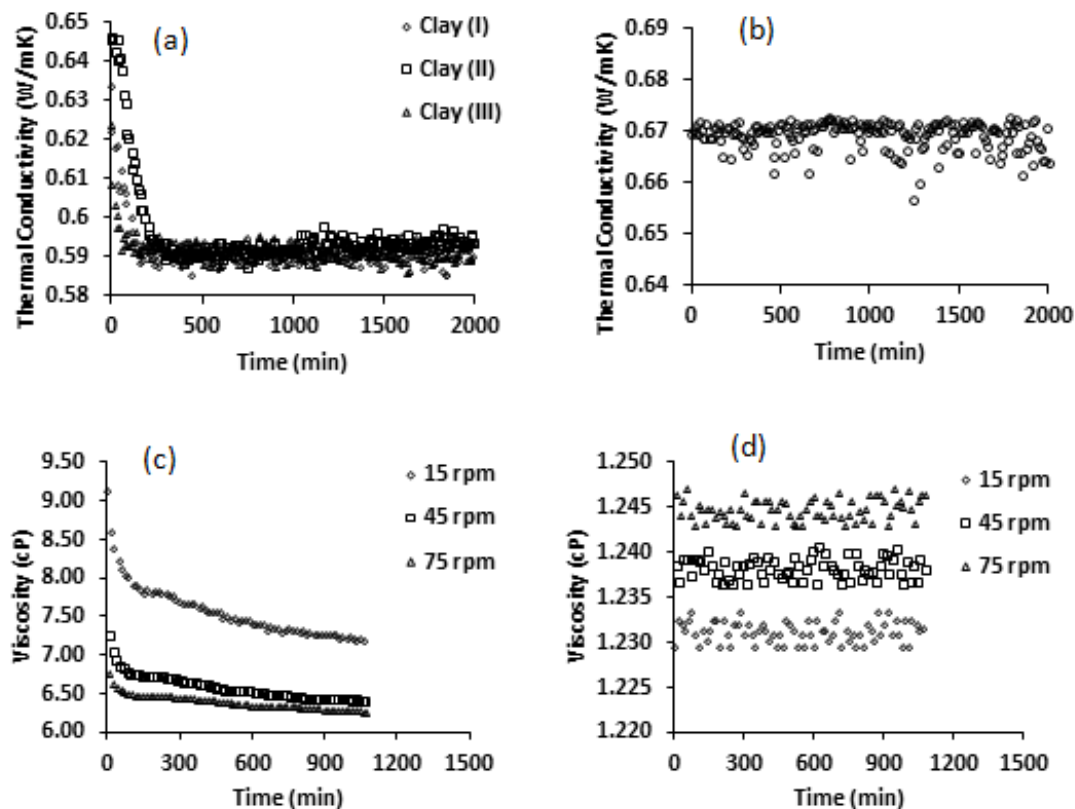
Figure 3.4 TC measurement results for **(a)**: clays (I), (II) and (III); **(b)** Al_2O_3 NFs and viscosity measurement results for **(c)** CeO_2 NFs (9 wt%) in W/EG (50% Vol) and **(d)**: Al_2O_3 NFs (paper 2)

measurement, and negligible changes for the viscosity of Al_2O_3 NF are observed at different rpms. The increase in viscosity of ~23.5% was observed compared to the viscosity value of water at 20˚C. These experiments clearly revealed the importance of stability on thermo-physical properties of NFs. On the other hand it emphasized us to fabricate NFs with higher stability. Therefore and at the next stage a plan was designed for obtaining the NFs with higher stability by using the method of steric stabilization for dispersing the nanostructured materials in the base liquid rather than electrostatic stabilization ($MPSiO_2$ NFs). It means that surface modifiers were selected and used to modify the surface of nanostructured materials which could result in higher stability of NFs. For this purpose Multi walled carbon nanotubes (CNTs) was selected and attempts were done to stabilize CNTs in water as base liquid. Due to the hydrophobic surface, they cannot be stabilized in the water media without surface modification. Triton X-100 (TX) and Gum Arabic (GA) were two suitable surface modifiers which were selected for stabilizing CNTs in water. To study the effect of heat treatment and formulate NFs with desired thermo-

physical and higher stability properties, as-received CNT (AR-CNT) was heated at 300 ^{o}C for 2 hours. Then both AR-CNTs and heat treated CNT (HT- CNTs) with 0.1 wt% concentration were dispersed and stabilized in water using TX and GA surface modifiers. Different concentration of two surface modifiers was used to find the optimum amount of surface modifiers so that fabricated NFs were stable for several months without observing material sedimentation. Then
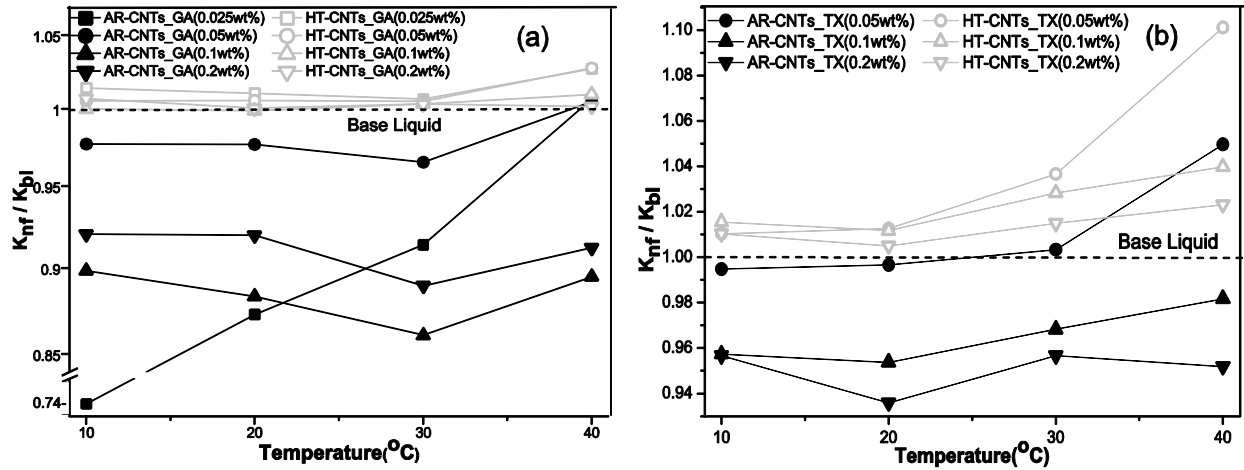

Figure 3.5 TC measurement on **(a)** GA (0.025-0.2 wt%) modified and **(b)** TX (0.05-0.2 wt %) modified AR- and HT-CNTs (0.1 wt%) at various temperatures (paper 3)

the TC of NFs was measured using THW method for both NF systems including AR-CNTs and HT- CNTs modified with TX and GA in different temperature from 10 ^{o}C to 40 ^{o}C. The results are shown in figure 3.5 (a) and (b) and based on these figures the heat treatment of AR- CNT resulted in enhancement of TC of NFs. Moreover, the TC of NF with AR-CNTs as well as HT-CNTs was significantly affected by the concentration of surface modifiers. Based on figure 3.5 (a) for NFs modified by GA, the maximum TC enhancement of 2.75% was obtained with the concentration of 0.05 wt% GA at 40 ^{o}C. From the results presented in figure 3.5 (b) one can see that maximum TC enhancement of ~10.2% was obtained for the NF with HT-CNTs (0.1 wt%) modified by TX (0.05 wt%) at 40 ^{o}C. This value was the maximum TC enhancement among all AR- and HT-CNT NFs modified by TX and GA. As a result NFs with HT- CNTs exhibited an enhancement of 4.8% and 2% after modification using TX and GA; respectively, compared to the NFs containing AR- CNTs. Moreover, NFs with TX surface modifier showed higher TC compared to the GA modified NFs for both suspensions containing AR- CNT and HT- CNTs. The rheological behavior of NFs was also studied for all NF systems at 20 ^{o}C. The results are

presented in figure 3.6. At low share rate NFs show high viscosity and the viscosity decreases as shear rate increases. Moreover based on figure 3.6, the increase in viscosity for NF containing HT- CNTs is lower than that of AR –CNTs indicating the positive effect of heat treatment on viscosity of NFs. NFs with TX as surface modifier showed lesser increased viscosity compared to the same NFs with GA. The minimum and maximum values for increased viscosity
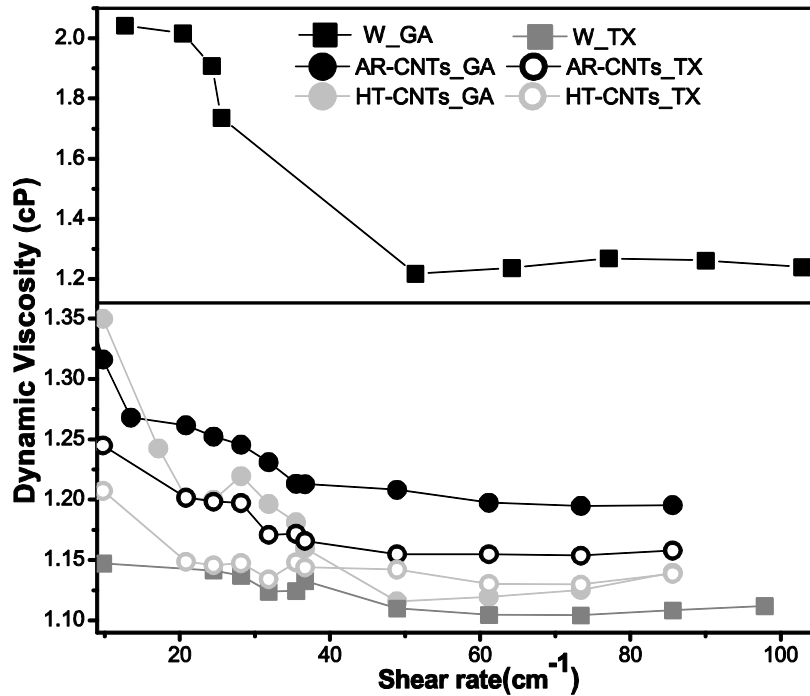

Figure 3.6 Dynamic viscosity vs shear rate for NFs containing AR- and HT-CNTs (0.1 wt%) modified using TX and GA at 20 °C (paper 3)

(2% and 9.5%) were obtained for the NFs containing HT- CNTs modified by TX and AR- CNTs modified by GA, respectively. Therefore, the NF containing HT-CNT (0.1 wt%) modified by TX (0.05 wt%) displayed the optimal thermo-physical properties with ~10.2% TC enhancement while only 2% increase in viscosity indicating its capability for using in cooling applications. In other words, combination of surface modification and heat treatment of CNT resulted in preparation of stable water based CNT NFs with desired dispersion and improved thermo-physical properties.

3.2 Effect of particle size and preparation methods on thermo-physical properties of NFs (Appended paper 4 and 5)

One of our aims in this work was to study the effect of particle size and NF preparation method on thermo-physical properties of NFs including TC and viscosity. In this section we summarize our findings regarding these important factors by fabrication/synthesis of copper NFs with DEG as base liquid using one-step and two-step preparation methods. To study the role of particle size on TC and viscosity of NFs, commercial copper nanoparticles (Cu NPs) and copper microparticles (Cu MPs) with the particle size in the range of (20-40 nm) and (0.5-1.5µm) were purchased. Then a two-step method (figure 2.1) was used to fabricate the DEG based Cu NFs and copper microfluids (Cu MFs) with the concentration of 1, 2 and 3wt%. The use of surface modifier was avoided to observe the real effect of particles on thermo-physical properties of NFs/MFs. Due to inconsistency in the literature as well as our experiences in dealing with NFs made by low viscosity base liquids, where formulated NFs showed different thermo-physical
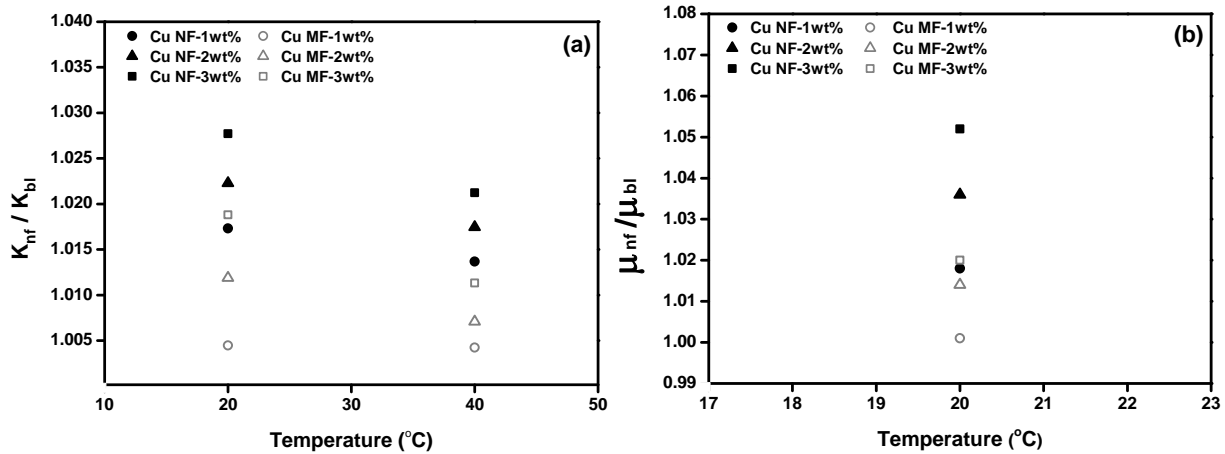

Figure 3.7 (a) Relative TC of NFs/MFs at different Cu particle concentration and temperatures; **(b)** Relative viscosity of NFs/MFs with various Cu particle concentrations at 20 ^{o}C (paper 4)

characteristics and made the effect of particle inconclusive, we decided to use a base liquid with higher viscosity. Therefore DEG was selected and used as the base liquid. Selection of DEG as base liquid was the novelty in this study since there was no report in the literature on using DEG with suspended Cu NPs/MPs (Cu NF/Cu MF) as heat transfer fluid. To study the thermo-physical properties of Cu NFs/MFs, fabricated samples with various concentrations of 1, 2 and 3wt% were tested for their TC using TPS method and viscosity. TC was measured at 20 ^{o}C and

40 ^{o}C while viscosity was tested only at 20 ^{o}C. The relative TC and viscosity results for all NFs/MFs are presented in the figure 3.7 (a) and (b), respectively. All NFs/MFs showed higher TC over the base liquid. Based on figure 3.7 (a) the TC enhancement of NFs/MFs were increased by increase of particle concentrations. The TC enhancements for NFs were higher than the values for MFs; may be due to higher surface area in Cu NPs compared to the MPs. The maximum TC enhancement of around 2.8% was observed for NF with 3wt% Cu NP at 20 ^{o}C. Regarding the rheological behavior, all NFs/MFs showed Newtonian behavior. The relative viscosity values are displayed in figure 3.7 (b) and based on that viscosity of all NFs/MFs increased as Cu NPs/MPs was increased. Moreover, Cu NFs exhibited higher viscosity values compared to the Cu MFs may be due to larger contact area between copper NPs and DEG base liquid. By comparing figures 3.7 (a) and (b) it can be seen that NF with 3wt% Cu NP, although showed 2.8% TC enhancement at 20 ^{o}C, it exhibited 5.2 % increase in viscosity at the same temperature. In fact for all NFs the TC enhancements were lower than the increased in viscosity values. It indicated that although this NF showed some TC enhancement, having significant increase in its viscosity did not let us to go forward; it must be optimized to be considered as a candidate for heat transfer applications. To study the effect of NF preparation method on thermo-physical properties, Cu NFs was also directly synthesized in DEG as base liquid via microwave-assisted method (as one-step preparation method). It should be mentioned that although there are several one-step NFs preparation methods, due to some restrictions such dispersion quality and the cost of product in these conventional methods, developing new way to avoid these limitations is needed. The microwave-assisted heating method could be a proper option because the reagents and solvents are heated uniformly in microwave system which leads to accelerate the nucleation of metal clusters as well as produce monodispersed nanostructured materials. Although there are few studies in the literature on the preparation of Cu NPs in DEG [170], they have not been evaluated for their thermo-physical properties. Therefore, in this section the fabrications of Cu NFs via microwave-assisted one-step method and for the first time, evaluation of their thermo-physical properties (experimentally and theoretically) are presented. Our aim also was to investigate the role of preparation method on thermo-physical properties for Cu NFs by comparison between two NFs systems fabricated via one-step and two-step method. For these purposes Cu NF was synthesized via microwave-assisted method and characterized for their physico-chemical and thermo-physical properties. In order to evaluate the thermo-physical

properties of Cu NFs, several NFs with different concentrations of 0.4 wt%, 0.6 wt%, 0.8 wt% and 1.6 wt% were made (section 2.1). The TC tests were done for the all Cu NFs with DEG as base liquid using TPS method in the temperature range between 20 ^{o}C and 50 ^{o}C. The figure 3.8 (a) shows the relative TC evaluation results and based on that the TC of NFs was increased by increase of Cu NP concentration and the maximum TC enhancement of ~7.2 % was achieved for Cu NFs with 1.6 wt% Cu NPs concentration at 20 ^{o}C.
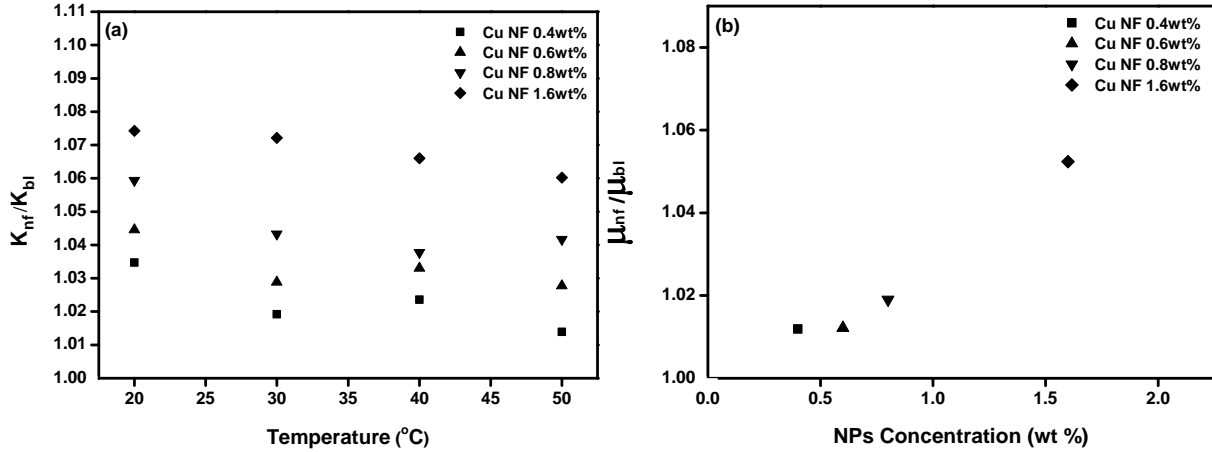

Figure 3.8 (a) Relative TC of Cu-DEG NFs with various Cu NPs concentration at different temperatures.; **(b)** Relative viscosity of Cu-DEG NFs with various concentration of Cu NPs between 0.4wt% and 1.6wt% at 20 ^{o}C (paper 5)

Other attempt was done to study the rheological behavior of the Cu NFs and the NFs showed Newtonian behavior. Figure 3.8 (b) shows the relative viscosity evaluation results for the all NFs at 20 ^{o}C. It shows that the viscosity of NFs increases as the Cu NP concentration increases and based on that the maximum increase of ~5.2% in viscosity was observed for the Cu NF with 1.6 wt% Cu NPs concentration. From comparison between figure 3.8 (a) and (b) one can clearly see that in the all NFs prepared by one-step method the TC enhancement is greater than the increase in viscosity for all samples at 20 ^{o}C while in the two-step method the reverse trend was observed. It means that based on figure 1.7 NFs prepared by one-step method may be useful for some industrial application where there is no issue about pressure drop. We also compared our results achieved for Cu NFs prepared using two-step and one-step method. Due to the different NPs concentration for both NF systems (one-step and two-step methods), DLS size for NFs cannot be compared directly and discuss about the impact of DLS size on thermo-physical properties of NFs achieved from two-step and one-step methods is not so accurate. The results for thermo-

physical properties for both DEG based NFs systems including one-step and two-step prepared NFs are presented in figure 3.9 (a) and (b). As can be seen from figure 3.9 (a), the highest TC enhancement among all samples including two-step and one-step fabrication methods was obtained for NF with 1.6wt% Cu NPs fabricated by one-step method at 20 $^{\circ}$C. Although at a particle concentration of only around half of that of the most concentrated NF prepared by the two-step method. Figure 3.9 (b) displays a comparison between the viscosities of the Cu NFs fabricated via two-step and one- and methods. The NF containing 3wt% Cu NPs (two step method) and 1.6wt% Cu NPs (one step method) have shown nearly the same viscosity may be due to the presence of chemicals with similar concentration in samples made by one-step method. The NFs with highest concentrations in both methods showed almost the same the increase in viscosity, while the TC enhancement was observed almost 2.5 times higher for the sample with 1.6wt% Cu NPs (one-step method). Therefore, NFs fabricated by the developed one-step method showed more enhanced thermal performance even at almost 50% of the concentration of NFs prepared via the two-step method.
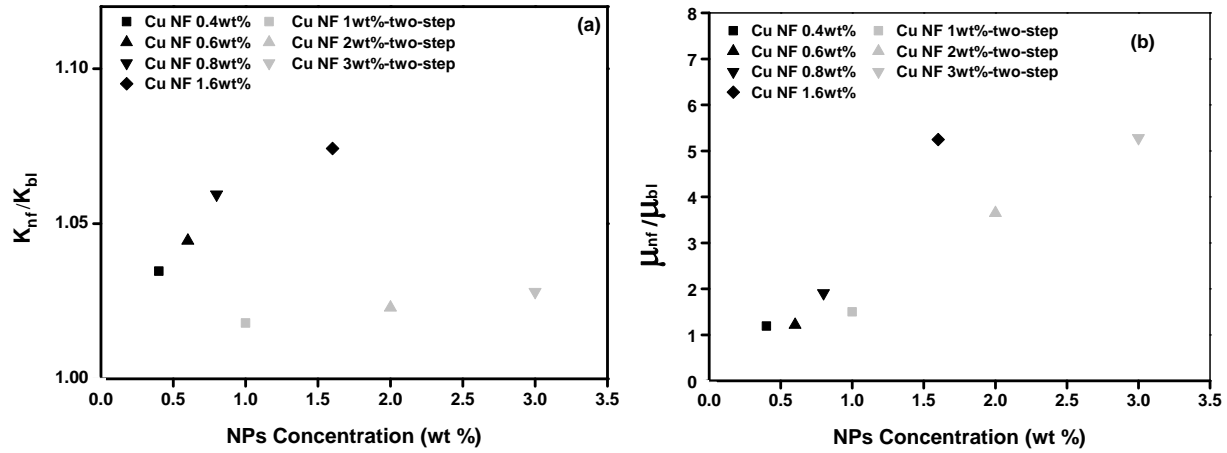

Figure 3.9 (a) Relative TC, and (**b**) Relative viscosity at 20 $^{\circ}$C for Cu-DEG NF with various Cu NPs concentration prepared using two-step and one step microwave-assisted method (paper 5)

Additionally, the NF with lowest Cu NPs concentration prepared by one-step method (Cu NF 0.4wt%) showed around 12% TC enhancement more than the NF with highest Cu NPs concentration fabricated by two-step method (Cu NF 3wt%- two-step). It indicates the effect of using microwave-assisted route as a suitable one-step synthesis method which can result in enhancing thermal performance of NFs.

3.3. Effect of NP crystal structure and base liquid on thermo-physical properties of NFs (Appended paper 6 and 7)

Few studies have been reported in the literature on the use of SiC NF for heat transfer applications [116,122, 176-178]; however, a comparative study on the effect of SiC crystal structure on the thermo-physical properties of NFs containing α-SiC and β-SiC NPs has not been done yet. Hence, the new set of experiments were designed by preparing NFs containing SiC particles with two different crystal structures to study comparatively the effect of crystal structure of SiC particles on thermo-physical properties of NFs. For this purpose a series of W/EG based NFs with 9wt% SiC particle concentration were fabricated by using the commercial α-SiC and β-SiC particles (figure 2.1). The summary of information for SiC NFs assisted in this study is listed in the table 3.2.

Table 3.2 SiC NFs evaluated for thermo-physical properties in this study

Sample	NP ID	Crystal Structure	Base Liquid (50:50) by wt%	NPs loading (wt %)	Surface Area* (m^2/g)
α1-SiC NF-W/EG	(α1-SiC)	Hexagonal	W/EG	9	18
α2-SiC NF-W/EG	(α2-SiC)	Hexagonal	W/EG	9	18
β1-SiC NF-W/EG	(β1-SiC)	Cubic	W/EG	9	80
β2-SiC NF-W/EG	(β2-SiC)	Cubic	W/EG	9	90

* Data provided by the supplier.

Figure 3.10 (a) shows β-SiC crystal structure which has a cubic crystal structure and it is formed at temperatures below 1700 °C, while as Figure 3.10 (b) displays, α-SiC NPs which are formed at temperatures higher than 1700 °C, possess a hexagonal crystal structure [179]. X-ray powder diffraction (XRD) analysis was carried out to determine the crystal structure of SiC NPs. Figure 3.10 (c) illustrates the XRD pattern of β1-SiC and β2-SiC NPs. The diffraction peaks at 35.8^o, 41.5^o, 60.0^o, 72.0^o and 75.7^o could be indexed as the (111), (200), (220), (311) and (222) reflections of β-SiC phase, respectively. (JCPDS#01-074-2307). There is a small amount of α-SiC phase which can be seen at the peak of 34.5^o. An excess silicon phase was observed in β2-SiC sample which was indexed with Si reference pattern (JCPDS#00-027-1402). Figure 3.10 (d) shows the XRD patterns for α1- and α2-SiC NPs where both types of α-SiC show hexagonal

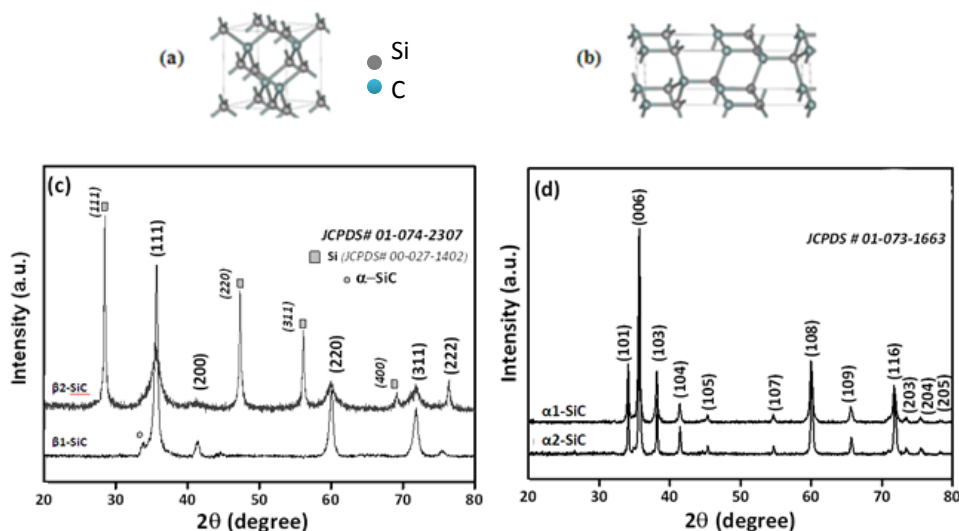crystal structure and all obtained peaks were indexed for hexagonal SiC phase (JCPDS # 01-073-1663).

Figure 3.10 The crystal structure and XRD pattern of **(a, c)** β1 and β2-SiC and **(b, d)** α1 and α2-SiC particles, respectively (paper 6)

In order to study the surface chemistry of SiC NPs, FTIR analysis was performed for all "as-received" SiC NPs and results are illustrated in figure 3.11 (a). The absorption band between 860 cm^{-1} and 760 cm^{-1} is due to the presence of Si-C bond. For all SiC NPs, the absorption from 1100 cm^{-1} to 1000 cm^{-1} are attributed to the Si-O-Si or Si-O-C vibrations, respectively. For α1-SiC particles the band at 1200 cm^{-1} is attributed to the Si-C. α2-SiC particles show absorption bands at 1180 cm^{-1} and 1380 cm^{-1}, which could be due to the Si-C and amorphous Carbon, respectively. Furthermore, there are two bands from 1525 to 1620 cm^{-1}, for both α1-SiC and α2-SiC particles, because of the C=O groups, which may be due to the residual chemicals or un-reacted precursor due to their fabrication method. By looking at β1-SiC, in addition to Si-C bond Si-O-Si at 780 and 1050 cm^{-1} respectively, there are two more bands at 1200 and 1315 cm^{-1}. The first band is attributed to Si-C and the second one to amorphous Carbon, respectively. Therefore, as the FT-IR analysis revealed SiC NPs have dissimilar surface chemistry characteristics which may affect the thermo-physical as well as dispersion properties for NFs containing SiC particles with different crystal structures. As discussed before to achieve stable NFs, the pH of a NF must be far from IEP, where the overall charge on the NPs becomes zero. In order to determine the stability region and optimum pH values for fabricating stable NFs, zeta potential analysis was

carried out for both α-SiC and β-SiC particles, in the pH region between 2 and 10 and the results are presented in figure 3.11 (b).
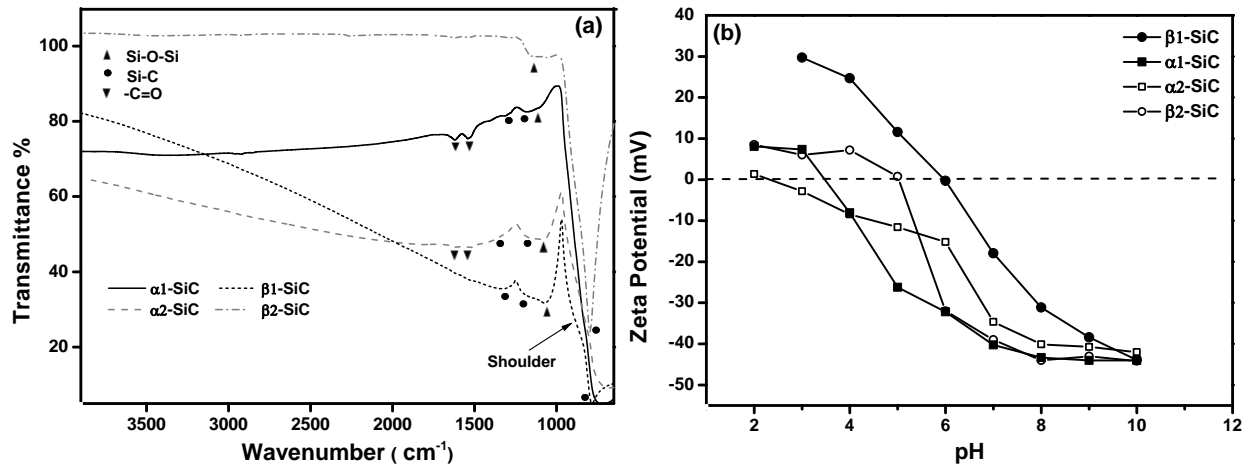

Figure 3.11 (a) FTIR spectra of as-received β- and α- type SiC particles; **(b)** the zeta potential analysis of α-SiC and β-SiC NPs as a function of pH (paper 6)

From zeta potential analysis, the IEP achieved for α-SiC and β-SiC particles show great variations, one very important common point of exhibiting highly negatively charged particles in the pH region of ~9.5-10. Hence, for obtaining stable suspensions, the pH of NF samples was adjusted at 9.5. Figure 3.11 (b) also shows that β-SiC NPs has higher IEP values compared to the α-SiC. β1-SiC and β2-SiC particles have very close IEP values in the pH range of 5-6, while α-SiC NPs exhibit similar IEP values in the pH range of 2-3. The possible reasons for these results may be because of different synthesis route for SiC particles, and presence of impurities which can lead to different surface chemistry of α-SiC and β-SiC particle. As FT-IR analysis showed (figure 3.11 (a)), different SiC NPs revealed different surface chemistry. By comparing FT-IR results with zeta potential analysis, it can be seen that obtaining lower IEP for α2-SiC than α1-SiC may be due to higher silica content of α2-SiC, which shifts the IEP to more acidic pH region. β2-SiC NPs exhibit slightly lower IEP than β1-SiC NPs: Although β2-SiC showed higher Si-O-Si bands in FTIR, it exhibited a lower IEP due to probably the high content of Si (assessed from XRD). To evaluate thermo-physical properties of NFs, first TC of W/EG based NFs containing 9wt% of SiC with different crystal structures were measured using TPS method at 20 $^{\circ}$C and the results are listed in the table 3.3. The NFs showed higher TC values compared to the base liquid. The TC values for NFs with α-SiC particles are higher compared to the NFs containing β-SiC

NPs; may be because of different crystal structure of SiC NPs since they have also dissimilar TC values [180] (490 W/m.K for α-SiC and 360 W/m.K for β-SiC). Sample impurities may also result in different TC values where XRD and FT-IR clearly revealed the presence of impurities and dissimilar surface chemistry for the SiC particles. As a result and at the same particle loading, NF containing α1-SiC with TC enhancement of 20% and β2-SiC with TC enhancement of 7% showed the highest and lowest TC among the all NFs, respectively. The viscosity of all NFs with W/EG as the base liquid was measured at 20 ^{o}C, where all the NFs showed Newtonian behavior. The results are also listed in table 3.3. Based on those NFs with α- type SiC particles have lower viscosity values compared to the NFs with β- type SiC particles. The effect of the crystal structure or the level of impurities (observed from XRD and FTIR analysis) or different particle primary sizes for α-SiC and β-SiC (from BET) can be some possible reasons. As one can see from the table 3.3 at the same particle loading, the NFs containing α2-SiC and β2-SiC NPs with increase in viscosities of 12% and 60% showed the lowest and highest values among the all NFs, respectively; may be due to having smallest and largest surface area.

Table 3.3 TC and viscosity evaluation results of SiC NFs tested at 20 ^{o}C

Sample	NPs loading (wt %)	TC W/mK	K_{nf}/K_{bl}	Viscosity (cP)	μ_{nf}/μ_{bl}
Base Liquid (W/EG)	-	0.392	-	3.897	-
α1-SiC NF-W/EG	9	0.4704	1.20	4.4425	1.14
α2-SiC NF-W/EG	9	0.4626	1.18	4.3646	1.12
β1-SiC NF-W/EG	9	0.4469	1.14	5.299	1.36
β2-SiC NF-W/EG	9	0.4195	1.07	6.2352	1.60

Our findings for α1-SiC NF-W/EG show favorable thermo-physical properties (higher TC enhancement with lower increase in viscosity) compared to all series of water and W/EG based α-SiC NFs reported in the literature [116,122,176-178]. The reason is not clear yet, however, the type of base liquid, the different surface chemistry of α-SiC particles, additives or different NPs concentrations can be some possible reasons. As mentioned before the trade off between thermo-

physical properties including relative viscosity values and relative TC is significant for utilizing the NFs for heat transfer applications. Figure 3.12 summarizes the comparison between TC
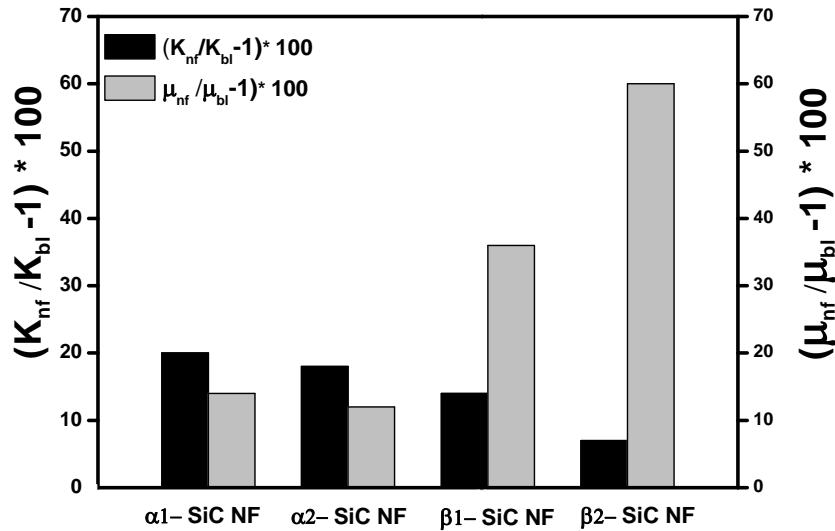

Figure 3.12 Comparison between the TC enhancement and increase in viscosity at 20 $^{\circ}$C for NFs, with W/EG as base liquid, containing 9 wt% α- and β- type SiC particles (paper 6)

enhancement and viscosity increase, for all fabricated α- and β-SiC NFs. Both α-SiC NFs showed that their TC increase is higher than the viscosity increase at 20 $^{\circ}$C, while reverse behavior was obtained for β-SiC NFs. This may mean that NFs formulated using α-SiC particles can be suitable candidates as efficient NFs for convective heat transfer applications. Furthermore, a comparison between α1-SiC NF and α2-SiC NF indicated that although α1-SiC NF showed 2% higher viscosity increase, it showed 2% more TC enhancement value indicating a promising capability of this NF as efficient heat transfer fluid. As among all SiC NFs presented in this section, NFs containing α1-SiC particle showed the optimal thermo-physical properties, therefore, it was selected for additional thermal characteristics investigations. Our final aim was to select the NF with optimal TC and viscosity properties for convective heat transfer tests. For this reason, at this stage not only the effect of α1-SiC particle concentration was studied, but also the base liquid effect –as one of the most important factor affecting the thermo-physical properties of NFs- was considered. For these purposes, a series of α1-SiC NFs with two base liquids (distilled water and W/EG 50:50 weight ratio) and containing various α1-SiC particles (3, 6 and 9wt%) were fabricated. The preparation procedure has been expressed in figure 2.1. The information about the fabricated NFs with various particle concentration and different base

liquids have been listed in table 3.4. For the all listed α1-SiC NFs, the thermo-physical properties evaluation including TC and viscosity measurements were performed at 20 ^{o}C and the results are

Table 3.4 Detailed information for prepared α1-SiC NFs

Sample ID	NP ID	Base Liquid	NP loading	
			(vol %)	(wt %)
α1-SiC NF-W/EG-3wt%	α1-SiC NP	W/EG (50:44.5) by vol%	0.95	3
α1-SiC NF-W/EG-6wt%	α1-SiC NP	W/EG (50:44.5) by vol%	1.9	6
α1-SiC NF-W/EG-9wt%	α1-SiC NP	W/EG (50:44.5) by vol%	2.85	9
α1-SiC NF-W-3wt%	α1-SiC NP	Distilled water	0.95	3
α1-SiC NF-W-6wt%	α1-SiC NP	Distilled water	1.9	6
α1-SiC NF-W-9wt%	α1-SiC NP	Distilled water	2.85	9

displayed in figure 3.13 (a)-(d). Figure 3.13 (a) shows the relative TC of water based α1-SiC NFs at 20 ^{o}C for different particle concentration, indicating minimum and maximum TC enhancement of 1% and ~15.2 % for NFs with 3 wt% and 9 wt% particle concentration at 20 ^{o}C, respectively. Figure 3.13 (b) displays the relative viscosity of water based α1-SiC NFs at 20 ^{o}C where a maximum and minimum increase of ~22.7 % and 4.7 % in viscosity was obtained for 9 wt% and 3wt% α1-SiC NF, respectively. Figure 3.13 (c) presents the relative TC at 20 ^{o}C, showing minimum and maximum TC enhancement of ~ 9.2% and 20 % for W/EG based NFs with 3 wt% and 9 wt% particle concentration, respectively. Finally figure 3.13 (d) illustrates the relative viscosity for W/EG based α1-SiC NFs at 20 ^{o}C, which clearly indicates that the viscosity changes in parallel to the NP concentration. The minimum and maximum increase of ~ 6.8% and 14% in viscosity was achieved for α1-SiC NFs containing 3 wt% and 9 wt% particle concentration, respectively. To have an easier conclusion for selecting the NF with optimal thermo-physical properties for the final stage (HTC test), the TC and viscosity values of α1-SiC NFs with different base liquids, as water and W/EG mixture, at different α1-SiC particles concentration are summarized in figures 3.14 (a) and (b). Based on figure 3.14 (a), NFs with DW/EG base liquid result in ~5% - 8% higher TC enhancements than water at the same particle concentration. NFs with DW/EG base liquid indicate much lower increase in viscosity except for

NF at particle concentration of 3wt% as displayed figure 3.14 (b). Furthermore, at the same particle concentration, water based SiC NFs display ~ 2% -7% higher increase in viscosity
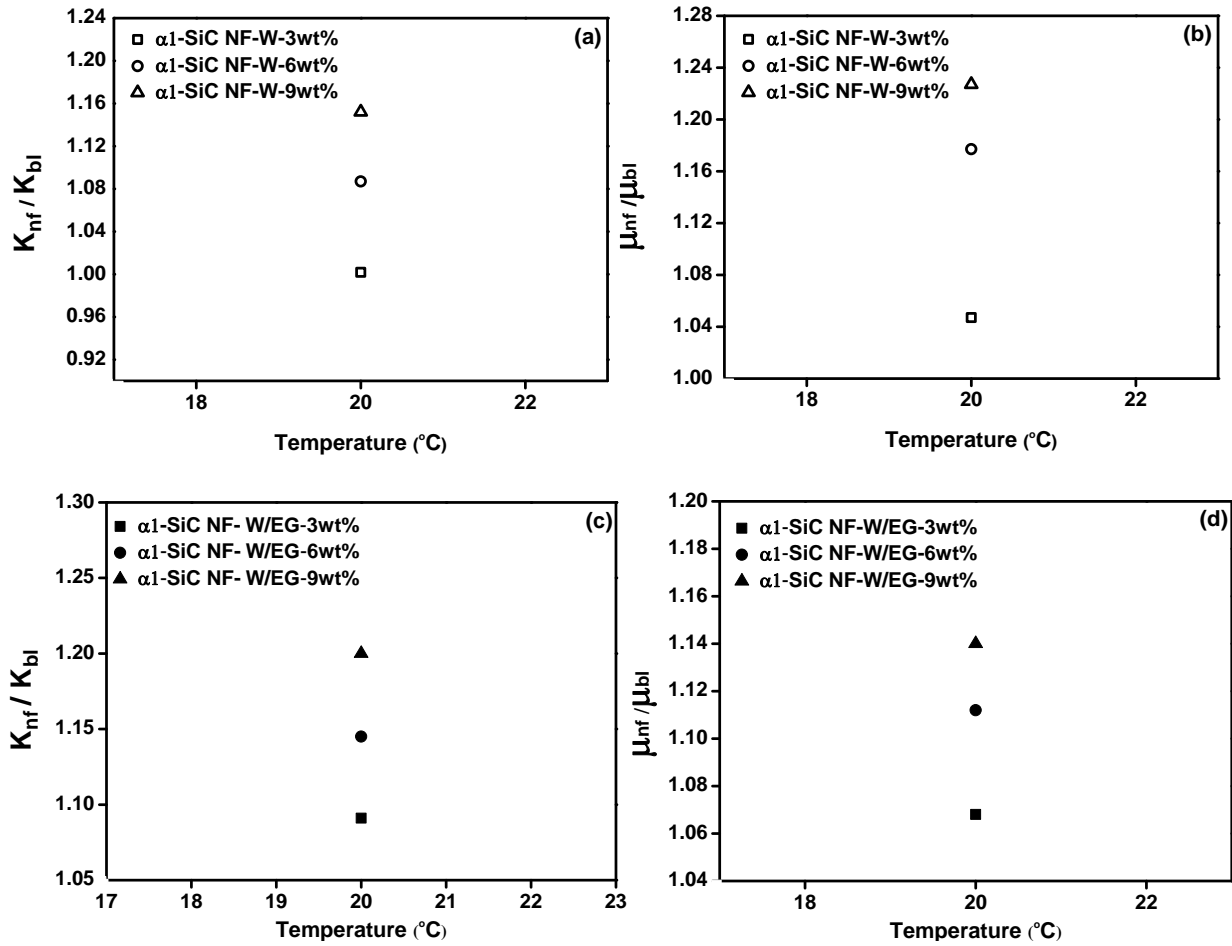

Fig. 3.13 Thermo-physical property evaluation of α1-SiC NFs with various α1-SiC NPs concentration: **(a)** Relative TC of water based NFs, **(b)** Relative viscosity of water based NFs, **(c)** Relative TC of W/EG based NFs and **(d)** Relative viscosity of W/EG based NFs (all values are recorded at 20 °C) (paper 7)

values than the NFs in W/EG base liquid at 6 wt% and 9 wt% particle loading. It means that if water is selected as the base liquid, a higher pumping power will be required for heat transfer applications. W/EG based NFs showed higher efficiencies compared to the similar distilled water based NF, as heat transfer fluid, due to the effect of the base liquid. Therefore, it can be a suitable candidate for performing HTC tests to see its capacity for being effective heat transfer fluid.
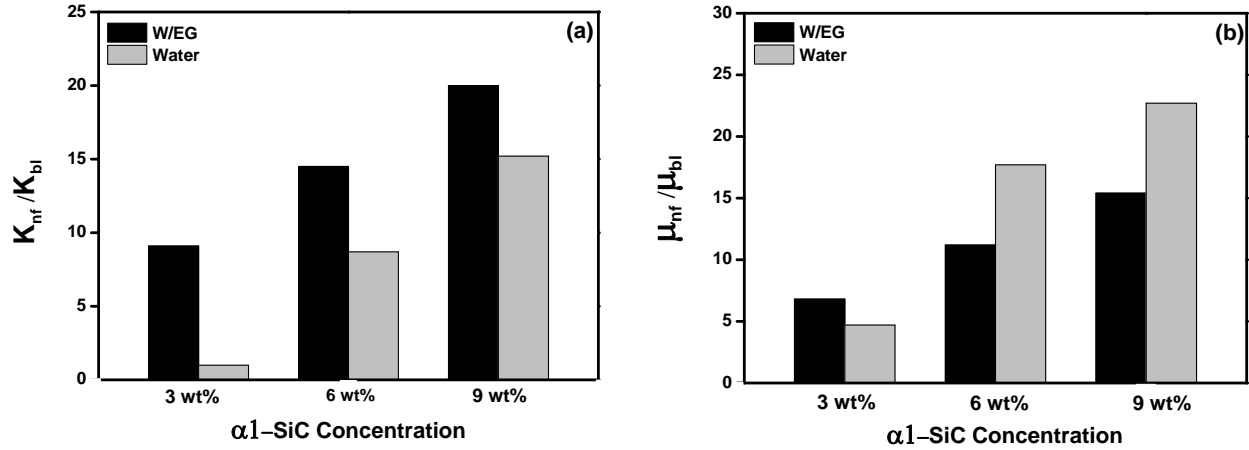
Figure 3.14 Comparison of the change in **(a)** TC, and **(b)** Viscosity of SiC NFs with DW and DW/EG as base liquids and various particles loading of α1-SiC NPs at 20 ^{o}C (paper 7)

3.4 Proof of concept demonstration of enhanced NFs heat transfer (Appended paper 7)

As we showed, among all water and W/EG based α1-SiC NFs with various concentration, W/EG based NF containing 9 wt% α1-SiC particles (α1-SiC NF-W/EG-9wt%) exhibited a promising thermo-physical properties. It indicates the potential of this NF for utilizing as efficient heat transfer fluid in practical applications. Therefore, at this stage HTC tests were designed and performed for this promising NF, in order to evaluate the capacity of this NF for practical convective heat-transfer applications. HTC evaluation can be performed and compared using different criteria such as equal Reynolds number, mass flow rate, and pumping power. However, comparing the results at equal Reynolds number may be misleading [181-182]. NFs have higher viscosity than the base liquids; therefore, a higher flow rate (higher velocity) is desired to have the same Reynolds number for NFs as the base liquid. A more realistic comparison of HTC performance is at constant pumping power, velocity, or flow rate. Therefore, the HTC tests were done in three mentioned different criteria for α1-SiC NF containing 9wt% particle loading. Figure 3.15 shows a comparative graph for HTC evaluation of the NF for those three criteria. In all evaluation criteria NF performed significantly better than the base liquid in the HTC tests. Specifically the achieved enhancements are; 13% at equal Reynolds number, 8.5% at equal volume flow and 5.5% at equal pumping power. This reveals promising characteristics for this NF for use in convective heat transfer applications. Now we compare the obtained thermo-physical (TC and viscosity) and transport (HTC) properties results for α1-SiC NF-DW/EG-9wt%

with the flow chart presented in figure 1.7. As one can see this NF is the only case that could pass the all stages and barriers successfully so that it can be used as effective heat transfer fluid.
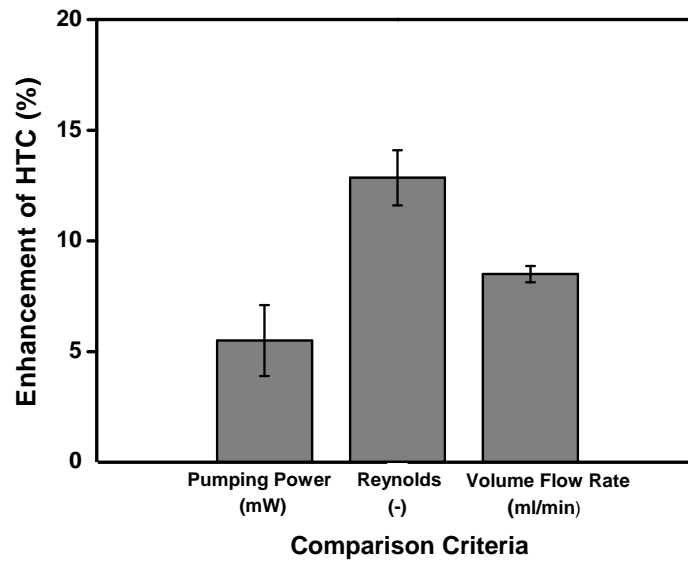

Figure 3.15 Comparative analysis of experimental results (HTC vs. pumping power, Reynolds number and volume flow rate) for α1-SiC NF-DW/EG-9wt%

4. Summary and Conclusions

In this work we focused on fabrication, physico-chemical, thermo-physical and heat transfer characteristics evaluation of NFs. Our major effort was preparing efficient NFs with optimal properties for heat transfer applications. The final NFs should not only show a good stability and optimal thermo-physical properties (high TC enhancement with minimal impact of NPs on viscosity) but also exhibit the best heat transfer performance. The thermo-physical properties of NFs are influenced by several factors such as composition and concentration of nanostructured materials, base liquid, NP morphology (size and shape), NF preparation method, pH of suspension, stability, temperature and surface modifiers. Therefore, in the first stage, detailed studies were carried out to engineer NFs with good stability and optimal thermo-physical properties. Particular investigation for the first time was devoted to study the role of particle crystal structure on thermo-physical properties of NFs. For this purpose, several NFs were fabricated using different nanostructured materials and various base liquids via one-step and two-step methods. To have a better control for achieving the final goal, an optimization procedure was designed to check the desired characteristics for each NF system in the related stages.

We developed, for the first time, novel water based NFs using $MPSiO_2$ particle via a two-step method. Although these NF systems showed some promising TC enhancement, they exhibited poor stability and high viscosity values. We then focused on the stability of NF, as a significant factor affecting the thermo-physical properties of NFs, by evaluating and improving the stability of NFs. In this section a simple method was developed and used to evaluate the stability of NFs. The role of stability on viscosity and TC of some commercial NFs were studied showing significant effect of stability on thermo-physical properties of NFs. In the next step, the stability of NFs was enhanced using appropriate surface modifiers. For this purpose, CNTs were stabilized in water using TritonX-100 (TX) and Gum Arabic (GA) as surface modifiers. The results showed that not only the heat treatment and composition of surface modifier influence the thermo-physical properties of NFs but also the concentration of surface modifiers play a significant role. A maximum TC enhancement of ~10.2 % with increase in viscosity of ~ 2% was obtained for TX modified HT-CNT NFs at 40 ^{o}C.

The role of particle size and preparation method on TC and viscosity of NFs were studied on Cu as the model system. DEG based Cu NF systems containing different concentration and size of Cu NPs and MPs were fabricated using a two-step method. The results showed that TC of NFs

was higher than that of MFs while the viscosity of NFs showed higher values compared to the MFs; may be due to the large contact area between Cu NPs and DEG base liquid. The maximum TC enhancement of ~ 2.8 % was obtained for Cu NFs with 3wt% Cu NPs at 20 $^{\circ}$C while the increase in viscosity of 5.2% was achieved for the same NF at the same temperature. For these NF systems the TC increase was lower than the increase in viscosity values indicating that although some enhancement was obtained for NFs at high concentration, they still need to be optimized for use as heat transfer fluid.

To study the effect of preparation method on thermo-physical properties of NFs, microwave-assisted one-step preparation method was used. Several DEG based Cu NFs with various Cu NP concentrations were prepared and evaluated for their thermo-physical properties. In all Cu NFs prepared by one-step method, the TC enhancement values were higher than the increase in viscosity, indicating their potential for use in some industrial applications. A comparison between one-step and two-step methods preparation of DEG based Cu NFs revealed the higher TC enhancement for NFs made by one step method even at lower Cu NPs concentration.

To demonstrate the effect of particle crystal structure on the thermo-physical properties of NFs a series of experiments were designed with SiC as the model system. For this task a two-step method was used to fabricate W/EG based NFs (9wt%) using SiC particles with two different crystal structures of α- and β. The results revealed that NFs with α-SiC has higher TC compared to β-SiC, may be due to the effect of crystal structure (as α-type has higher TC value). Among all W/EG based suspensions with α- and β-SiC particles, the NF containing α1-SiC particle showed the highest TC enhancement of 20%, while only 14% increase in viscosity, indicating its promising characteristics for heat transfer applications. This sample was selected as the best case with optimal thermo-physical properties among all NFs studied during this work. Therefore, it was considered for further evaluation, where HTC tests were carried out for different criteria in a laminar flow regime. A HTC enhancement of 5.5% at equal pumping power as realistic criteria was achieved for this NF indicating its capability for use in practical and industrial heat transfer applications.

In conclusion, although there are a lot of studies in literature reporting about NFs performance for heat transfer applications, our findings are among the very first studies where the thermo-physical and transport properties of NFs were studied in detail in different aspects. The final

HTC result was noticeable, reproducible and based on a practical situation showing the capability of our engineered NFs to commercialize as effective heat transfer fluid.

5. Future Work

We plan to perform more detailed work on NF containing α-SiC particles, especially on the case that showed the highest TC (α1-SiC NF) by focusing on viscosity property of these NFs. Our aim will be further reduction of viscosity of these NFs with no negative impact on TC. Using proper surface modifiers with optimum concentration may result in reduction of the NFs viscosity. We will continue the work on W/EG based NFs with SiC NPs by enhancing the phase purity of the as-received materials. It can assist us to have a better understanding about the effect of crystal structure on thermo-physical properties of NFs. Moreover, we will evaluate the capability and performance of α1-SiC NFs in some real applications such as microchannels or IGBTs. As there were a lot of contradictions in the literature regarding the effect of particle size (primary size, aggregated size etc.) on thermo-physical properties of NFs, we plan to do a systematic work using α-SiC NPs in different size to study the size effect on TC and viscosity of NFs. The one-step preparation method especially microwave assisted route as an efficient method for preparation of NFs, will be continued. For example in Cu-DEG NF systems prepared by microwave-assisted method replacing other stabilizer may result in better dispersion which may enhance the thermo-physical properties of NFs. Preparation of NFs using microwave-assisted one-step method can be continued for making NFs with different nanostructured materials and various base liquids in order to achieve stable NFs with desired thermo-physical properties.

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References

1. A S Ahuja, *J Appl Phys*, 46 (1975), 3408

2. K V Liu, S U S Choi, K E Kasza, Report No. ANL -88-153, 1988

3. C Buzea, I I Pacheco, K Robbie, *Biointerphases,* 2 (2007), MR 17

4. C N R Rao, A Muller, A K Cheetham, The Chemistry of Nanomaterials: Synthesis, Properties and Applications, Wiley-VCH,Weinheim, 2004

5. G M Whitesides, B Grzybowski, *Science* 295 (2002) , 2418

6. W A Lopes, H M Jaeger, *Nature,* 414 (2001), 735

7. S Chung, D S Ginger, M W Morales, Z Zhang, V Chandrasekhar, M A Ratner, C A Mirkin, *Small* 1(2005), 64

8. D Mijatovic, M Fujita, M S Dresselhaus, *Phys Rev B*, 54 (1996),17954

9. G Cao, Nano structure and Nanomaterials – Synthesis, Properties and Applications, Imperial College Press, UK, 2004

10. M Wilson, K Kannangara, G Smith, M Simmons, B Raguse, Nanotechnology: Basic Science and Emerging Technologies, Chapman & Hall/CRC, New York, 2002

11. Nanotechnology for energy applications, www.nano-connect.org

12. S US Choi, *ASME FED*, 231 (1995), 99

13. L G Asirvatham, R Nimmagadda, S Wongwises, *Int J Heat and Mass Transf,* 60 (2013), 201

14. M K Aliabadi, F Hormozi, A Zamzamian, *Exp Therm Fluid Sci*, 52 (2014), 248

15. L S Sundar, M K Singh, I Bidkin, A C M Sousa, *Int J Heat and Mass Transf,* 70 (2014) , 224

16. H J Kim, I C Bang, J Onoe, *Opt Laser Eng*, 47 (2009) 532

17. T K Hong, H S young, C J Choi, *J Appl Phys*, 97 (2005), 064311

18. J Albadr, S Tayal, M Alasadi, *Case Studies in Thermal Engineering,* 1 (2013), 38

19. B Rahmati, A A D Sarhan, M Sayut, *J Clean Prod*, 66 (2014), 685

20. Y Vermahmoudi, S M Peyghambarzadeh, S H Hashemabadi, M Naraki, *Eur J Mech B/Fluids*, 44 (2014), 32

21. L Syam Sundar, M K Singh, A C M Sousa, *Int Commun Heat Mass*, 49 (2013), 17

22. M T Naik, G R Janardana, L S Sundar, *Int Commun Heat Mass*, 46 (2013), 13

23. A A Abbasian Arani, J Amani, *Exp Therm Fluid Sci*, 44 (2013), 520

24. W H Azmi, K V Sharma, P K Sarma, R Mamat, S Anuar, V D Rao, *Exp Therm Fluid Sci*, 51 (2013), 103

25. A K Tiwari, P Ghosh, J Sarkar, *Appl Therm Eng*, 57 (2013), 24

26. M T Zafarani-Moattar, R Majdan-Cegincara, *Fluid Phase Equilibr*, 354 (2013), 102

27. A Tadjarodi, F Zabihi, S Afshar, *Ceram Int*, 39 (2013), 7649

28. S L Song, J H Lee, S H Chang, *Exp Therm Fluid Sci*, 52 (2014), 12

29. B Deepthi, H C Barshilia, K S Rajam, M S Konchady, D M Pai, J Sankar, *Surf Coat Tech*, 205 (2010), 1937

30. X Xu, H Li, G Xian, *Mater Lett*, 66 (2012), 176

31. S S Gupta, V M Siva, S Krishnan, T S Sreeprasad, P K Singh, T Pradeep, S K Das, *J Appl Phys,* 110 (2011), 084302

32. S D Park, S W Lee, S Kang, In Cheol Bang, Ji Hyun Kim, Hyeon Suk Shin, D W Lee, D W Lee, *Appl Phys Lett,* 97 (2010), 023103

33. Z Sun, S Pöller, X Huang, D Guschin, C Taetz, P Ebbinghaus, J Masa, A Erbe, A Kilzer, W Schuhmann, M Muhler, *Carbon*, 64 (2013), 288

34. E Ettefaghi, H Ahmadi, A Rashidi, A Nouralishahi, S S Mohtasebi, *Int Commun Heat Mass*, 46 (2013), 142

35. S M Alves, B S Barros, M F Trajano, K S B Ribeiro, E Moura, *Tribol Int*, 65 (2013), 28

36. R S Khedkar, A S Kiran, S S Sonawane, K Wasewar, S S Umre, *Procedia Engineering*, 51 (2013), 342

37. M N Rashin, J Hemalatha, *Exp Therm Fluid Sci*, 48 (2013), 67

38. M Kole, T K Dey, *Exp Therm Fluid Sci*, 35 (2011), 1490

39. W Yu, H Xie, L Chen, Y Li, *Colloid Surface A*, 355 (2010), 109

40. S M Hashemi, M A Akhavan-Behabadi, *Int Commun Heat Mass*, 39 (2012), 144

41. D Tripathi, O A BégNano-cryosurgery, *Int J Heat and Mass Transfer*, 70 (2014), 61

42. K V Wong, O D Leon, *Advances in Mechanical Engineering*, 2010 (2009), 1

43. A V Kuznetsov, *Fluid Dyn Res,* 43 (2011), 055505

44. I Sharifi, H Shokrollahi, S Amiri*, J Magn Mater,* 324 (2012), 903

45. L Hendraningrat, S Li, O Torsæter, *J Petrol Sci Eng,* 111 (2013), 128

46. B A Suleimanov , F S Ismailov, E F Veliyev, *J Petrol Sci Eng,* 78 (2011) 431

47. J S Nam, P Lee, S W Lee, *Int J Mach Tools Manuf,* 51 (2011), 649

48. S Gu, Y Zhang, B Yan*, Mater Lett*, 97 (2013), 169

49. H T Phan, N Caney, P Marty, S Colasson, J Gavillet, *Nanosc Microsc Therm*, 14 (2010), 229

50. D T Wasan, A D Nikolov, *Nature Int Wkly J Sci,* 423 (2003), 156

51. A Kosmala, Q Zhang, R Wright, P Kirby, *Mater Chem Phys,* 132 (2012), 788

52. Y Gan, Y S Lim, L Qiao, *Combust Flame*, 159 (2012), 1732

53. P Keblinski, J A Eastman, D G Cahill, *Mater Today*, 8 (2005), 36

54. S Senthilraja, M Karthikeyan, R Gangadevi, *Nano-Micro Lett*, 2 (2010), 306

55. S M Peyghambarzadeh, S H Hashemabadi, M S Jamnani, S M Hoseini, *Appl Therm Eng*, 31 (2011), 1833

56. S Khandekar, M Ravi Sankar, V Agnihotri, J Ramkumar, *Mater Manuf Process*, 27 (2012), 963

57. V Vasu, K M Kumar, *Nano-Micro Lett,* 3 (2011), 209

58. M Mital, *Appl Therm Eng*, 52 (2013), 321

59. W Yu, H Xie, *J Nano Mat*, 2012 (2011), 1

60. M Karami, M A Akhavan Bahabadi, S Delfani, A Ghozatloo , *SOL Energ Mat Sol C*, 121 (2014), 114

61. A A Abbasian Arani, J Amani, *Exp Therm Fluid Sci*, 42 (2012), 107

62. W Yu, H Xie, L Chen, Y Li, *Thermochimica Acta*, 491 (2009), 92

63. G Lee, C K Kim, M K Lee, C K Rhee, S Kim, C Kim, *Thermochim Acta,* 542 (2012), 24

64. S A Kumar, K S Meenakshi, B R V Narashimhan, S Srikanth, G Arthanareeswaran, *Mate Chem Phys,* 113 (2009), 57

65. J A Eastman, S U S Choi, S Li, W Yu, L J Thompson, *Appl Phys Lett*, 78 (2001), 718

66. H Zhu, Y Lin, Y Yin, *J Colloid Interf Sci,* 277 (2004), 100

67. A Ghadimi, R Saidur, H S C Metselaar, *Int J Heat Mass Transfer,* 54 (2011), 4051

68. D Zhu, X Li, N Wang, X Wang, J. Gao, H. Li, *Curr Appl Phys,* 9 (2009), 131

69. X J Wang, D S Zhu, S Yang, *Chem Phys Lett*, 470 (2009), 107

70. J C Chou, L P Liao, *Thin Solid Films*, 476 (2005), 157

71. J Huang, X Wang, influence of pH on the stability characteristics of nanofluid, IEEE Symposium on Photonics and Optoelectronics, 2009, 1-4, doi: 10.1109/SOPO.2009.5230102

72. L Jiang, L Gao, J Sun, *J Colloid Interface Sci*, 260 (2003), 89

73. V Iranidokht, S Hamian, N Mohammadi, M B Shafii, *Int J Therm Sci*, 74 (2013), 63

74. B Sahin, G G Gültekin, E Manay, S Karagoz, *Exp Therm Fluid Sci*, 50 (2013), 21

75. M Drzazga, E Kostrzewa, A Gierczycki, *Chem Eng Process*, 31 (2010), 387

76. E Tombácz, D Bica, A Hajdú, E Illés, A Majzik, L Vékás, *J Phys Condens Matter*, 21 (2008) 204103

77. N Du, S E Song, W G Hou, *Colloid Surface A*, 312 (2008), 104

78. K S Suganthi, K S Rajan, *Int J Heat Mass Transfer*, 55 (2012), 7969

79. H Peng, G Ding, H Hu, *Exp Therm Fluid Sci*, 35 (2011), 960

80. N S Souza, A D Rodrigues, C A Cardoso, H Pardo, R Faccio, AW Mombru, J C Galzerani, O F de Lima, S Sergeenkov, F M Araujo-Moreira, *Phys Lett A*, 376 (2012), 544

81. M N Pantzali, A A Mouza, S V Paras, *Chem Eng Sci,* 64 (2009) 3290

82. A Indhuja, K S Suganthi, S Manikandan, K S Rajan, *J Taiwan Inst Chem Eng*, 44 (2013), 474

83. J W Lee, Y T Kang, *Energy,* 53 (2013), 206

84. T Yousefi, E Shojaeizadeh, F Veysi, S Zinadini, *Sol Energy*, 86 (2012), 771

85. P Esmaeilzadeh, N Hosseinpour, A Bahramian, Z Fakhroueian, S Arya, *Fluid Phase Equilibr*, 361 (2014), 289

86. J Zeng, F R Zhu, S B Yu, Z L Xiao, W P Yan, S H Zheng, L Zhang, L X Sun, Z Cao, *Sol Energ Mat Sol C*, 114 (2013), 136

87. T Parametthanuwat, S Rittidech, A Pattiya, Y Ding, S Witharana, *Nanoscale Res Lett,* 6 (2011), 315

88. X Xu, Z Yu, Y Zhu, B Wang, *Diam Relat Mater,* 14 (2005), 206

89. P Gurav, S S Naik, K Ansari, S Srinath, K A Kishore, Y P Setty, S Sonawane*, Colloid Surface A*, 441 (2014), 589

90. M S Saterlie, H Sahin, B Kavlicoglu, Y Liu, O A Graeve, *Chem. Mater*, 24 (2012), 3299

91. D Wu, H Zhu, L Wang, L Liua, *Curr Nanosci,* 5 (2009), 103

92. S Mukherjee, S Paria, *IOSR Journal of Mechanical and Civil Engineering (IOSR-JMCE)*, 9 (2013), 63

93. Y Li, J E Zhou, S Tung, E Schneider, S Xi, *Powder Technol*, 196 (2009), 89

94. Y Hwang, J K Lee, J K Lee, Y M Jeong, S Cheong, Y C Ahn, S H Kim, *Powder Technol*, 186 (2008) 145

95. H Zhu, C Zhang, Y Tang, J Wang, B Ren, Y Yin, *Carbon,* 45 (2007), 226

96. J H Lee, K S Hwang, S P Jang, B H Lee, J H Kim, S U S Choi, C J Choi, *Int J Heat Mass Transfer*, 51 (2008), 2651

97. Manoj N, S K Dwivedi, G Agrwal, *Int J Pharm Research Sci*, 2 (2013), 662

98. X Li, D Zhu, X Wang , *J Colloid Interface Sci*, 310 (2007), 456

99. B P Singh, R Menchavez, C Takai, M Fuji, M Takahashi, *J Colloid Interface Sci*, 291 (2005), 181

100. C C Li, Chang M H, *Mater Lett,* 58 (2004), 3903

101. Y Hwang, J K Lee, C H Lee, Y M Jung, S I Cheong, C G Lee, B C Ku, S P Jang, *Thermochim Acta,* 455 (2007), 70

102. H Yoshida, H Masuda, K Fukui, Y Tokunaga, *Adv Powder Technol*, 12 (2001), 79

103. H Xie,J Wang, T Xi, Y Liu, F Ai, Q Wu, *J Appl Phys,* 91 (2002) , 4568

104. D Lee, J W Kim, B G Kim, *J Phys Chem B*, 110(2006), 4323

105. D H Yoo, K S Hong, T E Hong, J A Eastman, H S Yang, *J Korean Phys Soc,* 51 (2007), S84

106. R Karthik, R Harish Nagarajan, B Raja, P Damodharan, *Exp Therm Fluid Sci,* 40 (2012), 1

107. M J Assael, I N Metaxa, J Arvanitidis, D Christofilos, C Lioutas, *Int J Thermophys*, 26 (2005), 647

108. M Drzazga, G Dzido, M Lemanowicz, A Gierczycki, Influence of nonionic surfactant on nanofluid properties, 14th European Conference on Mixing, Warszawa, Sep 10-13, 2012

109. K Wusiman, H Jeong, K Tulugan, H Afrianto, H Chung, *Int Commun Heat Mass,* 41 (2013), 28

110.   A Ghozatloo, M Shariaty-Niasar, A M Rashidi, *Int Commun Heat Mass,* 42 (2013), 89

111.   W Yu, D M France, Jules L Routbort, S U S Choi, *Heat Transfer Eng*, 29 (2008), 432

112.   H Masuda, A Ebata, K Teramae, N Hishinuma, *Netsu Bussei*, 7 (1993), 227

113.   L Fedele, L Colla, S Bobbo, *Int J Refrig*, 35 (2012), 1359

114.   M Moosavi, E K Goharshadi, A Youssefi, *Int J Heat and Fluid Flow,* 31 (2010), 599

115.   H Q Xie, J C Wang, T G Xi, Y Liu, F Ai, *J Mater Sci Lett*, 21 (2002), 1469

116.   E V Timofeeva, W Yu, D M France, D Singh, J L Routbort, *J Appl Phys*, 109 (2011), 014914

117.   T P Teng, Y H. Hung, T C Teng, H E Mo, H G Hsu, *Appl Therm Eng*, 30 (2010), 2213

118.   M Chopkar, S Sudarshan, P K Das, I Manna, *Metall Mater Trans A*, 39 (2008), 1535

119.   X Wang, X Xu, S U S Choi, *J Thermophys Heat Transfer*, 13(1999), 474

120.   J Hong, D Kim, *Thermochim. Acta*, 542 (2012), 28

121.   C Wu, T Joon , J Xu, D Lee, B Yang, M Zachariah M, *Phys Rev E*, 81 (2010), 011406/1

122.   H Xie, J Wang, T Xi, Y Liu, *Int J Thermophys,* 23 (2002), 571

123.   S M S Murshed, K C Leong, C Yang, *Int J Therm Sci*, 44 (2005) 367

124.   M M Elias, I M Shahrul, I M Mahbubul, R Saidur, N A Rahim, *Int J Heat Mass Transfer*, 70 (2014), 289

125.   J Jeong, C Li, Y Kwon, J Lee, S H Kim, R Yu, *Int J Refrig*, 36 (2013), 2233

126.   E K Goharshadi, H Ahmadzadeh, S Samiee, M Hadadian, *Phys Chem Res*, 1 (2013), 1

127.   A Nasiri, M Shariaty-Niasar, A Rashidi, A Amrollahi, R Khodafarin, *Exp Therm Fluid Sci*, 35 (2011), 717

128.   A Ghadimi, I H Metselaar, *Exp Therm Fluid Sci*, 51 (2013), 1

129.   J Y Jung, C Cho, W H Lee, Y T Kang, *Int J Heat Mass Transfer*, 54 (2011), 1728

130.   L Yang, K Du, Effect of dispersion stability on thermal conductivity of binary nanofluids, International Conference on Remote Sensing, Environment and Transportation Engineering, 2011, 4935–8, doi: 10.1109/RSETE.2011.5965419

131.   R Cheung, Silicon carbide microelectromechanical systems for harsh environments, Imperial College Press, UK, 2006

132.   G Paglia, Determination of the Structure of γ-Alumina using Empirical and First Principles Calculations Combined with Supporting Experiments, Ph.D. Thesis, Curtin University of Technology, Perth, Retrieved 2009-05-05, 2004

133.   N Nikkam, M Saleemi, E B Haghighi, M Ghanbarpour, R Khodabandeh, M Muhammed, B Palm, M S Toprak, *Nano-Micro Lett.*, 6 (2014), 178

134.   J J De Groot, J Kestin, H Sookiazian, *Physica*, 75 (1974), 454

135.   M Wan, R R Yadav, K L Yadav, S B Yadaw, *Exp Therm Fluid Sci*, 41 (2012), 158

136.   A Santucci, L Verdini, P G Verdini, *Rev Sci Instrum*, 57 (1986), 1627

137.   C Kleinstreuer, Y Feng, *Nanoscale Res Lett*, 6 (2011), 229

138.   J J De Groot, J Kestin, H Sookiazian, *Physica,* 75 (1974), 454

139.   Y Nagasaka, A Nagashima, *J Phys E*, 14 (1981), 1435

140.   J C Maxwell, A Treatise on Electricity and Magnetism, Clarendon Press, Oxford, UK, 1, (1873)

141.   R L Hamilton, O K Crosser, *IEC Fundam*, 1 (1962)

142.   R H Davis, *Int J Thermophys*, 7 (1986), 609

143.   D J Jeffrey, *Proc R Soc Lond Ser A*, 335 (1973), 355

144.   Q Z Xue, *Nanotechnology*, 17 (2006), 1655

145.   C Nguyen, F Desgranges, G Roy, N Galanis, T Mare, S Boucher, H A Mintsa, *Int J Heat Fluid Flow,* 28 (2007), 1492

146.   I M Mahbubul, R Saidur , M A Amalina, *Int J Heat Mass Transfer*, 55 (2012), 874

147.   Q Li, Y Xuan, J Wang, *Exp Therm Fluid Sci*, 30 (2005) 109

148.   M Drzazga, A Gierczycki, G Dzido, M Lemanowicz, *Chin J Chem Eng*, 21 (2013), 104

149.   E V Timofeeva, W Yu, D M France, D Singh, J L Routbort, *Nanoscale Res Lett*, 6 (2011), 182

150.   W Lu, Q Fan, *Eng Anal Boundary Elem,* 32 (2008), 282

151.   E V Timofeeva, D S Smith, W Yu, D M France, D Singh, J L Routbort, *Nanotechnology*, 21 (2010), 215703

152.   Y He, Y Jin, H Chen, Y Ding, D Cang, H Lu, *Int J Heat Mass Transfer*, 50 (2007), 2272

153.   R Prasher, D Song, J Wang, P Phelan, *Appl Phys Lett*, 89 (2006), 133108

154.   E V Timofeeva, J L Routbort, D Singh, *J Appl Phys*, 106 (2009), 014304

155.   H Chen, Y Ding, C Tan, *New J Phys*, 9 (2007), 367

156.   K B Anoop, S Kabelac, T Sundararajan, S K Das, *J Appl Phys*, 106 (2009), 034909

157.   Z Jia- Fei, L Z Yang, Ni M J, C K Fa, *Chinese Phys Lett,* 26 (2009), 066202

158.   T S Chow, *Phys Rev E*, 48 (1993), 1977

159.   H C Brinkman, *Chem Phys*, 20 (1952), 571

160.   G Batchelor, *J Fluid Mech*, 83 (1977), 97

161.   T S Lundgren, *J Fluid Mech*, 51 (1972), 273

162.   N Frankel, A Acrivos, *Chem Eng Sci*, 22 (1967), 847

163.   I M Krieger, T J Dougherty, *J Rheol*, 3 (1959) 137

164.   H Chen, Y Ding, Y He, C Tan, *Chem Phys Lett*, 444 (2007), 333

165.   Y M Xuan, Q Li, *J Heat Transf*, 125 (2003), 151

166.   B X Wang, L P Zhou, X P Peng, *Int J Heat Mass Transfer*, 46 (2003), 2665

167. R K Shah, Proc. 3rd National Heat Mass Transfer Conference. Indian Institute of Technology, Bombay, 1 (1975)

168. H Hausen, *Ver deut Ing, Beih. Verfahrenstechnik,* 4(1943), 91

169. K Stephan, M Abdelsalam, *Int J Heat Mass Transfer*, 23 (1980), 73

170. M Blosi, S Albonetti, M Dondi, C Martelli, G Baldi, *J Nanopart Res*, 13 (2011), 127

171. X Wang , Y Ma, R Raza, M Muhammed, B Zhu, *Electrochem Commun*, 10 (2008), 1617

172. E B Haghighi, Z Anwar, I Lumbreras, S A Mirmohammadi, M Behi, R Khodabandeh, B Palm, *J Phys Conf Ser*, 395 (2012), 012036

173. E B Haghighi, M Saleemi, N Nikkam, R Khodabandeh, M S Toprak, M Muhammed, B Palm, *Int Commun Heat Mass*, 52 (2014), 1

174. N Nikkam, E B Haghighi, M Saleemi, M Behi, R Khodabandeh, M Muhammed, B Palm, M S Toprak, *In Press in the Int Commun Heat Mass*, 2014

175. J Rouquerol, D Avnir, C W Fairbridge, D H Everett, J M Haynes, N Pernicone, J D F Ramsay, K S W Sing, K K Unger, *Pure Appl Chem*, 66 (1994), 1739

176. S W Lee, S D Park, S Kang, I C Bang, J Hs Kim, *Int J Heat Mass Transfer*, 54 (2011), 433

177. D Singh, E Timofeeva, W Yu, J Routbort, D France, D Smith, J M Lopez-Cepero, *J Appl Phys*, 105 (2009), 064306

178. E V Timofeeva, D S Smith, W Yu, D M France, D Singh, J L Routbort, *Nanotechnology*, 21 (2010), 215703

179. T Muranaka, Y Kikuchi, T Yoshizawa, N Shirakawa, J Akimitsu, *Sci Technol Adv Mater,* 9 (2008), 044204

180. R A Andrievski, *Rev Adv Mater Sci*, 22 (2009), 1

181. Y M Xuan, Q Li, *Trans ASME C*, 125 (2003), 151

182. W Yu, D M France, D S Smith, D Singh, E V Timofeeva, J L Routbort, *Int J Heat Mass Transfer*, 52 (2009), 3606