AN EXPERIMENTAL STUDY OF THE FLOW BOILING
OF REFRIGERANT-BASED NANOFLOUIDS

BY

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DISSETATION
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ABSTRACT

The use of nanofluids for various heat transfer applications has been a topic of intense research over the last decade. A number of studies to evaluate the thermophysical properties and single-phase heat transfer behavior of nanofluids have been reported. The current study is focused on the use of nanofluids in flow boiling applications, with CO₂ and R134a used as the base refrigerants. CuO nanoparticles 40nm in size, and TiO₂ nanoparticles 200nm in size are used to create partially stable CO₂-based nanofluids. Stable nanofluids are created in R134a by mixing it with dispersions of surface-treated nanoparticles in polyolester (POE) oil (RL22H and RL68H). The particles (Al₂O₃, ZnO, CuO, and ATO) at particle mass fractions from 0.08% to 1.34%, with particle sizes of 20nm and 40nm are coated with polar and non-polar surface treatments. The thermal properties of R134a-based nanofluids are measured. Thermal conductivity shows limited improvements; the largest increase of 13% is observed with CuO nanoparticles. Significant increases in viscosity, as high as 2147%, are observed due to CuO nanoparticles. Only the ATO nanofluid exhibited a decrease in the measured viscosity.

Heat transfer coefficients during flow boiling of nanofluids are measured over a range of mass flux from 100 to 1000 kg/m²s, with a heat flux from 5 to 25kW/m², and vapor quality up to 1. The test section is a smooth copper tube, 6.23mm in diameter and 1.8m in length. Average decreases of 5% and 28% are observed in heat transfer coefficients during flow boiling of CuO/CO₂ and TiO₂/CO₂ nanofluids, respectively. For the R134a-based nanofluids, average decreases in heat transfer during flow boiling at the highest particle mass fraction are 15% and 22% for Al₂O₃ and ZnO nanoparticles, respectively. CuO nanoparticles exhibit an average decrease of 7% for particle mass fraction of 0.08%. An average increase of 10% is observed with ATO nanoparticles at a 0.22% mass fraction. Heat transfer performance deteriorates with increase in viscosity and particle number density. The performance is also worse for partially stable nanofluids that modify the test section surface. Modifications to the thermophysical properties is the primary mechanism that affects heat transfer performance during flow boiling of nanofluids; increased thermal conductivity enhances while increased viscosity and surface tension reduce heat transfer in nucleate boiling-dominated flows. A secondary mechanism of nanoparticles filling up the micro-cavities on test surface is also responsible for decreased heat transfer and is a strong function of particle number density.
To my parents,
Ranjana and Dadasaheb Kolekar
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# TABLE OF CONTENT

LIST OF FIGURES .......................................................................................................................................... VIII
LIST OF TABLES ............................................................................................................................................... XI
LIST OF SYMBOLS ........................................................................................................................................... XII
LIST OF ACRONYMS ....................................................................................................................................... XV

CHAPTER 1: INTRODUCTION .............................................................................................................................. 1
  1.1 NANOPARTICLES .......................................................................................................................................... 1
  1.2 NANOFLUIDS ............................................................................................................................................... 2
  1.3 THERMOPHYSICAL PROPERTIES ............................................................................................................... 4
  1.4 TWO-PHASE FLOW ..................................................................................................................................... 6
  1.5 OBJECTIVES OF THE STUDY ...................................................................................................................... 7
    1.5.1 Novelty of the research ......................................................................................................................... 8
    1.5.2 Statement of objectives ....................................................................................................................... 8
  1.6 STRUCTURE OF THE THESIS ................................................................................................................... 9

CHAPTER 2: CO$_2$-BASED NANOFLUIDS ........................................................................................................... 10
  2.1 OVERVIEW ................................................................................................................................................ 10
  2.2 LITERATURE REVIEW ............................................................................................................................... 10
  2.3 EXPERIMENT DESIGN ............................................................................................................................... 16
    2.3.1 Apparatus .......................................................................................................................................... 16
    2.3.2 Procedure ......................................................................................................................................... 17
  2.4 EXPERIMENTAL APPROACH .................................................................................................................... 18
    2.4.1 Data analysis ...................................................................................................................................... 18
    2.4.2 R134a baseline data ........................................................................................................................... 19
    2.4.3 Experimental conditions ..................................................................................................................... 20
  2.5 RESULTS FROM CO$_2$-BASED NANOFLUIDS .......................................................................................... 20
    2.5.1 CuO/CO$_2$ nanofluid ......................................................................................................................... 20
    2.5.2 TiO$_2$/CO$_2$ nanofluid ......................................................................................................................... 21
    2.5.3 Baseline data after use of nanofluid ..................................................................................................... 24
  2.6 CONCLUSIONS .......................................................................................................................................... 24
CHAPTER 3: R134A-BASED NANOFLUIDS ................................................................. 34

3.1 OVERVIEW ................................................................................................. 34
3.2 LITERATURE REVIEW .............................................................................. 34
3.3 EXPERIMENT DESIGN .............................................................................. 39
  3.3.1 Apparatus ............................................................................................ 39
  3.3.2 Procedure ............................................................................................. 40
  3.3.3 Data analysis ....................................................................................... 42
  3.3.4 Experimental conditions ..................................................................... 43
3.4 THERMOPHYSICAL PROPERTIES OF NANOFLUIDS ................................. 43
3.5 BASELINE EXPERIMENTS ......................................................................... 45
3.6 RESULTS FROM R134A-BASED NANOFLUIDS ........................................ 50
  3.6.1 Al$_2$O$_3$/RL22H/R134a nanofluid ....................................................... 50
    3.6.1.1 Effect of particle mass fraction ....................................................... 50
    3.6.1.2 Effect of quality ............................................................................ 51
    3.6.1.3 Effect of particle size and particle number density ....................... 53
  3.6.2 ZnO/RL22H/R134a nanofluid ............................................................... 54
  3.6.3 CuO/RL68H/R134a nanofluid ............................................................... 55
  3.6.4 Al$_2$O$_3$/RL68H/R134a nanofluid ....................................................... 56
  3.6.5 ATO/RL68H/R134a nanofluid ............................................................... 57
3.7 CONCLUSIONS .......................................................................................... 59
3.8 FIGURES AND TABLES ................................................................................ 61

CHAPTER 4: PRESSURE DROP AND SUBCOOLING .............................................. 77

4.1 INTRODUCTION ......................................................................................... 77
4.2 PRESSURE DROP ...................................................................................... 77
4.3 CONDENSER SUBCOOLING ..................................................................... 80
4.4 FIGURES AND TABLES .............................................................................. 81

CHAPTER 5: CONCLUSIONS ............................................................................. 95

5.1 CO$_2$-BASED NANOFLUIDS ...................................................................... 96
5.2 R134A-BASED NANOFLUIDS ........................................................................................................ 96
5.3 RECOMMENDATIONS FOR FUTURE WORK .............................................................................. 97

REFERENCES ...................................................................................................................................... 99

APPENDIX A: DATA REDUCTION CODE .......................................................................................... 106

APPENDIX B: ADDITIONAL IMAGES FROM THE STUDY .............................................................. 114
LIST OF FIGURES

Figure 2.1: Schematic of the flow boiling apparatus................................................................. 26
Figure 2.2: Comparison of flow boiling heat transfer coefficients of R134a with models available
in literature .......................................................................................................................... 27
Figure 2.3: Comparison of a) $h$ and b) pressure drop in smooth copper tube for CuO/CO$_2$
nanofluid with baseline. ....................................................................................................... 28
Figure 2.4: Comparison of a) $h$ and b) pressure drop in smooth copper tube for TiO$_2$/CO$_2$
nanofluid with baseline. ....................................................................................................... 29
Figure 2.5: Variation in % change in $h$ for TiO$_2$/CO$_2$ nanofluid with mass flux at a) $q = 25$ kW/m$^2$
and b) $q = 5$ kW/m$^2$ ......................................................................................................... 30
Figure 2.6: Experimental conditions for data points from figure 2.5a represented on a) flow
regime map by Cheng et al. and b) modified flow regime map. Data points from left to right
correspond to those in figure 2.5a from right to left .............................................................. 31
Figure 2.7: Comparison of a) $h$ and b) pressure drop in smooth copper tube after the use of
nanofluids with baseline. ....................................................................................................... 32
Figure 3.1: Schematic of the flow boiling apparatus ................................................................. 61
Figure 3.2: a) TEM image of 40nm Al$_2$O$_3$ nanoparticles (courtesy of Nanophase Inc.) b) Image
of Al$_2$O$_3$/RL22H/R134a nanofluid through sight window of pressure vessel. ..................... 61
Figure 3.3: Comparison of flow boiling heat transfer coefficients of R134a with models available
in literature .......................................................................................................................... 62
Figure 3.4: a) Comparison of $h$ during flow boiling of RL22H/R134a mixture to pure R134a. b)
Variation of $h$ ratio with and without RL22H against quality ............................................. 63
Figure 3.5: a) Variation of $h$ ratio with and without RL68H against quality. b) Comparison of $h$
during flow boiling of different POE oil mixtures in R134a .................................................. 64
Figure 3.6: Heat transfer performance during flow boiling of Al$_2$O$_3$/RL22H/R134a nanofluid at
varying particle mass fraction ............................................................................................ 65
Figure 3.7: a) Variation in % change in $h$ with change in quality. b) Model predictions of
nucleate to convective boiling contributions for pure R134a ............................................. 67
Figure 3.8: Heat transfer performance during flow boiling of Al$_2$O$_3$/RL22H/R134a nanofluid at
different particle sizes and particle number densities .......................................................... 68
Figure 3.9: Heat transfer performance during flow boiling of ZnO/RL22H/R134a nanofluid at different particle sizes and particle number densities. .......................................................... 69
Figure 3.10: a) Heat transfer performance of 0.08% CuO nanofluid. b) Comparison of baselines before and after 0.08% CuO nanofluid experiment. ........................................................................ 70
Figure 3.11: a) Heat transfer performance of 0.22% CuO nanofluid. b) Comparison of baselines before and after 0.22% CuO nanofluid experiment. ........................................................................ 71
Figure 3.12: Heat transfer performance during flow boiling of Al₂O₃/RL68H/R134a nanofluid. 72
Figure 3.13: Heat transfer performance of ATO/RL68H/R134a nanofluid during a) flow boiling, b) convective heat transfer. ..................................................................................... 73
Figure 4.1: Pressure drop during flow boiling of a) CuO/CO₂ and b) TiO₂/CO₂ nanofluids. .... 81
Figure 4.2: Pressure drop during flow boiling of Al₂O₃/RL22H/R134a at different particle mass fractions.................................................................................................................. 82
Figure 4.3: Pressure drop during flow boiling of Al₂O₃/RL22H/R134a nanofluid at different particle sizes and particle number densities.......................................................... 84
Figure 4.4: Pressure drop during flow boiling of ZnO/RL22H/R134a nanofluid at different particle sizes and particle number densities.......................................................... 85
Figure 4.5: Pressure drop during flow boiling of CuO/RL68H/R134a nanofluid at different particle mass fractions........................................................................................................... 86
Figure 4.6: Pressure drop during flow boiling of a) Al₂O₃/RL68H/R134a and b) ATO/RL68H/R134a nanofluids.................................................................................................................. 87
Figure 4.7: Subcooling during condensation of a) CuO/CO₂ and b) TiO₂/CO₂ nanofluids in a brazed plate heat exchanger. .......................................................................................... 88
Figure 4.8: Subcooling during condensation of Al₂O₃/RL22H/R134a nanofluid at different particle mass fractions in a brazed plate heat exchanger. .................................................. 89
Figure 4.9: Subcooling during condensation of Al₂O₃/RL22H/R134a nanofluid at different particle sizes in a brazed plate heat exchanger. ............................................................... 91
Figure 4.10: Subcooling during condensation of ZnO/RL22H/R134a nanofluid at different particle sizes in a brazed plate heat exchanger. ............................................................... 92
Figure 4.11: Subcooling during condensation of CuO/RL68H/R134a nanofluid at different particle mass fractions in a brazed plate heat exchanger. .................................................. 93
Figure 4.12: Subcooling during condensation of a) Al$_2$O$_3$/RL68H/R134a and b) ATO/RL68H/R134a nanofluids in a brazed plate heat exchanger. .......................................................... 94

Figure B.1: Pressure vessel with measurement devices (image courtesy of Berghof Inc.). ..... 114

Figure B.2: Dispersion stability of a) CuO b) TiO2 nanoparticles in RL22H. ....................... 115

Figure B.3: a) Al$_2$O$_3$/RL22H dispersion with surface treatment 1 b) residue of the nanoparticles after stability test in R134a. .................................................................................. 116

Figure B.4: a) Al$_2$O$_3$/RL22H dispersion with surface treatment 2 b) residue of the nanoparticles after stability test in R134a. .................................................................................. 117

Figure B.5: a) Al$_2$O$_3$/RL22H dispersion with surface treatment 3 b) residue of the nanoparticles after stability test in R134a. .................................................................................. 118

Figure B.6: a) Al$_2$O$_3$/RL22H dispersion with surface treatment 4 b) residue of the nanoparticles after stability test in R134a. .................................................................................. 119

Figure B.7: a) Al$_2$O$_3$/RL22H dispersion with surface treatment 5 b) residue of the nanoparticles after stability test in R134a. .................................................................................. 120
LIST OF TABLES

Table 2.1: Experimental conditions for flow boiling of nanofluids........................................... 33
Table 2.2: Experimental uncertainty in recorded variables during flow boiling of nanofluids.... 33
Table 2.3: List of nanoparticles/dispersions tested for dispersion stability in CO₂..................... 33
Table 3.1: Experimental conditions for flow boiling of nanofluids........................................... 74
Table 3.2: Experimental uncertainty in recorded variables during flow boiling of nanofluids.... 74
Table 3.3: Thermal properties of nanofluids................................................................................. 75
Table 3.4: Combination of parameters to create nanofluids for the study................................. 76
LIST OF SYMBOLS

English Symbols

\( c_p \)  specific heat  \( (\text{kJ/kg-K}) \)
\( d \)  diameter of the tube  \( (\text{m}) \)
\( g \)  acceleration due to gravity  \( (\text{m/s}^2) \)
\( h \)  heat transfer coefficient  \( (\text{kW/m}^2\text{K}) \)
\( i \)  enthalpy  \( (\text{kJ/kg}) \)
\( k \)  thermal conductivity  \( (\text{W/m-K}) \)
\( L \)  length of the test section  \( (\text{m}) \)
\( m \)  mass  \( (\text{kg}) \)
\( P \)  pressure  \( (\text{kPa}) \)
\( \Delta P \)  differential pressure  \( (\text{kPa}) \)
\( \Delta P/L \)  pressure drop per unit length  \( (\text{kPa/m}) \)
\( Pr \)  Prandtl number
\( Q \)  heat transfer rate  \( (\text{kW}) \)
\( q \)  heat flux  \( (\text{kW/m}^2) \)
\( r_{cr} \)  critical radius  \( (\mu\text{m}) \)
\( r_i \)  inner radius  \( (\text{m}) \)
\( r_o \)  outer radius  \( (\text{m}) \)
\( Re \)  Reynolds number
\( T \)  temperature  \( (^\circ\text{C}) \)
\( \Delta T \)  temperature difference  \( (^\circ\text{C}) \)
\( V \)  velocity  \( (\text{m/s}) \)
\( %h \)  percentage change in \( h \)  \( (%) \)

Greek Symbols

\( \delta \)  liquid film thickness  \( (\text{m}) \)
\( \mu \)  viscosity  \( (\text{mPa-s}) \)
\( \rho \)  density  \( (\text{kg/m}^3) \)
σ  surface tension \((N/m)\)

Subscripts

exit  exit
\(f\)  fluid or liquid
\(fg\)  evaporation – fluid to gas
\(g\)  gas or vapor
\(in\)  inlet
\(Lt\)  total flow as liquid
\(ONB\)  onset of nucleate boiling
\(ref\)  refrigerant
\(sat\)  saturation
\(w\)  wall

Chemical formula

Ag  silver
\(Al_{2}O_{3}\)  aluminum oxide
\(ATO\)  antimony tin oxide
Au  gold
\(CO_{2}\)  carbon dioxide
Cu  copper
\(CuO\)  copper oxide
\(R113\)  1,1,2-trichlorotrifluoroethane \((C_{2}F_{3}Cl_{3})\)
\(R123\)  2,2-dichloro-1,1,1-trifluoroethane \((C_{2}HF_{3}Cl_{2})\)
\(R134a\)  1,1,1,2-tetrafluoroethane \((C_{2}H_{2}F_{4})\)
\(R141b\)  1,1-dichloro-1-fluoroethane \((C_{2}H_{3}FCl_{2})\)
\(R22\)  chlorodifluoromethane \((CHClF_{2})\)
\(R402A\)  R-125/290/22 (composition: 60\(\pm\)2/2\(\pm\)1/38\(\pm\)2)
\(R404A\)  R-125/143a/134a (composition: 44\(\pm\)2/52\(\pm\)1/4\(\pm\)2)
\(R502\)  R-22/115 (composition: 48.8/51.2)
\(R744\)  carbon dioxide
<table>
<thead>
<tr>
<th>Compound</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>$SiO_2$</td>
<td>silicon dioxide</td>
</tr>
<tr>
<td>$TiO_2$</td>
<td>titanium dioxide</td>
</tr>
<tr>
<td>$ZnO$</td>
<td>zinc oxide</td>
</tr>
</tbody>
</table>
# LIST OF ACRONYMS

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>AAD</td>
<td>average absolute deviation</td>
</tr>
<tr>
<td>cDAQ</td>
<td>compact data acquisition</td>
</tr>
<tr>
<td>CHF</td>
<td>critical heat flux</td>
</tr>
<tr>
<td>CNT</td>
<td>carbon nanotubes</td>
</tr>
<tr>
<td>COP</td>
<td>coefficient of performance</td>
</tr>
<tr>
<td>dc</td>
<td>direct current</td>
</tr>
<tr>
<td>EES</td>
<td>engineering equation solver</td>
</tr>
<tr>
<td>GWP</td>
<td>global warming potential</td>
</tr>
<tr>
<td>HCFC</td>
<td>hydrochlorofluorocarbon</td>
</tr>
<tr>
<td>HFC</td>
<td>hydrofluorocarbon</td>
</tr>
<tr>
<td>ISO</td>
<td>international organization for standardization</td>
</tr>
<tr>
<td>ODP</td>
<td>ozone depletion potential</td>
</tr>
<tr>
<td>POE</td>
<td>polyolester</td>
</tr>
<tr>
<td>PTFE</td>
<td>polytetrafluoroethylene</td>
</tr>
<tr>
<td>SUS</td>
<td>Saybolt universal second</td>
</tr>
<tr>
<td>VFD</td>
<td>variable frequency drive</td>
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</table>
CHAPTER 1: INTRODUCTION

1.1 Nanoparticles

Nanotechnology is the branch of technology that deals with manipulation of matter at atomic or molecular level. The manipulation is aimed at creating superior materials with better properties of interest. The use of this technology can lead to promising benefits in energy, healthcare, communication and other economic sectors.

Nanoparticles are in general particles with at least one primary dimension of less than 100nm. In some cases this dimension may be a few hundred nanometers. Nanoparticles exhibit considerably different properties than their bulk due to high surface to volume ratios. At these length scales size-dependent properties are observed in materials due to high percentage of atoms comprising the surface in comparison with the bulk of the material. Increased strength to weight ratios, better thermal and electrical conductivities, and improved optical/magnetic properties have been reported for nanoparticles. Pure metal, metal oxide, carbon and ceramic nanoparticles are available in market from different manufacturers. Nanoparticles are available in different shapes, sizes and also come surface treated for use in diverse applications. There are numerous uses of nanoparticles in both mundane and rare products that are encountered in daily life. These particles are used in the manufacturing of scratchproof glass, crack-resistant paints, anti-graffiti coatings, transparent sunscreens, stain repellent fabrics, and self-cleaning windows. They are being used in food industry to improve packaging, increase or decrease permeability in food products, and application of anti-microbial agents. Branches of medicines are using them as antioxidant agents, vaccine delivery systems, and protein delivery systems. These are only a few examples from a long list of applications in which nanoparticles are being used, and researchers are further investigating many others.

There are two main approaches in the manufacturing of nanomaterials. The “bottom up” approach relies on growth and self-assembly of single atoms and molecules to form nanostructures. This approach is very powerful in creating identical structures with atomic precision. The “top down” approach, on the other hand, relies on breaking down large-scale material to generate required nanostructures from them. This approach is superior for interconnectivity and integration that is very useful in electronic circuitry. To further distinguish
based upon processes used, nanoparticle manufacturing can be separated into six different categories [1]:

- Gas phase processes, including flame pyrolysis, high-temperature evaporation, and plasma synthesis
- Chemical vapor deposition (CVD)
- Colloidal or liquid phase methods
- Mechanical processes including grinding, milling, and alloying
- Atomic and molecular beam epitaxy
- Dip pen lithography

Safe handling of nanoparticles during manufacturing, downstream processes and common use is essential. Due to high surface to volume ratios, nanoparticles are very reactive and catalytic. Their interactions with biological systems are relatively unknown. Toxicity and human health effects of nanoparticles are also unknown and have been reported only in a few cases. Pulmonary inflammation, oxidative stress, and toxicological responses similar to asbestos have been reported due to exposure to nanoparticles in various animal studies. At present, there are no established regulatory exposure limits for nanomaterials in the United States. However, National Institute of Occupational Safety and Health (NIOSH) has released suggestions regarding engineering controls in nanomaterial production and downstream handling processes [1].

1.2 Nanofluids

Nanofluids are stable dispersions of nanoparticles in a base fluid. Most commonly used base fluids are water, glycols and oils. Research interest in nanofluids has gained significant momentum in the last decade due to their superior thermal properties. The research efforts are supplemented by access to variety of nanoparticles which is a result of advances in manufacturing. Nanofluids are much safer and easier to handle as end products compared to their constituent nanoparticles.

Most of the heat transfer fluids that are used in various applications have low thermal conductivity. Thermal conductivities of commonly used convective fluids like water and ethylene glycol at 25°C are 0.58 and 0.25W/m-K, respectively. Thermal conductivities of commonly used refrigerants like R134a and R22 at 10°C are 0.091 and 0.092W/m-K, respectively. Better thermal conductivity can lead to better heat transfer performance. Maxwell
conceptualized the approach of adding microparticles to fluid for improving its thermal conductivity in 19th century. Pure metal nanoparticles (Cu, Ag, and Au) and carbon nanotubes (CNT) are expected to have very high thermal conductivity ($\approx 500\text{W/m-K}$). However, these nanomaterials are costly. Thermal conductivity of commonly available and economically viable metal oxide nanoparticles is in the range of 10-40W/m-K which is still two orders of magnitude higher than the thermal conductivity of water. Thus, creating stable dispersions of nanoparticles in base fluids to improve thermal conductivity and thus heat transfer performance seems a logical approach.

Nanofluids are manufactured using two different techniques [2]. Two-step approach first creates nanoparticles and then disperses them into base fluid while a one-step approach simultaneously creates nanoparticles while dispersing them into fluid. Two-step approach is most commonly used in creating nanofluids and suffers from agglomeration of nanoparticles due to strong van der Waals force of attraction. Agglomeration of nanoparticles prevents stable nanofluids due to flocculation and settlement. One-step approach on the other hand is better for creating stable nanofluids; however, it is very costly and not economical for mass manufacturing. Thermal properties of nanofluids are very sensitive to the quality of the dispersion. Physical methods to break agglomerates such as stirring and ultrasonication are employed after creation of nanofluids using two-step approach. However, the ability of these methods to produce long term stable dispersions is questionable.

Various chemical techniques such as use of a stabilizing agent and surface treatment on nanoparticles are also used to stabilize the nanofluid. These stabilizing techniques can be characterized as follows:

- Electrostatic stabilization
  - Electrostatic repulsion force between the nanoparticles can be enhanced by increasing the thickness of electric double layer on the nanoparticle
  - Electrostatic repulsion competes with van der Walls force of attraction

- Steric stabilization
  - Non-ionic macromolecular surfactants are used to form a monomolecular layer on the nanoparticles
  - Provides steric hindrance among nanoparticles preventing flocculation and agglomeration
• Entropic stabilization
  – Polymer dissolved in the solvent acts as a stabilizing agent
• Dynamic stabilization
  – Stabilization under non-equilibrium working conditions
All the above techniques need to be customized for specific nanoparticle/base-fluid combinations based on their chemical interaction. Electrostatic stabilization is the favored technique for polar protic solvents while steric stabilization is better for polar aprotic and non-polar solvents.

The use of nanofluids in heat transfer applications is in its nascent stage. Thermal properties of nanofluids have been measured and are available in the literature. Convective heat transfer of nanofluid has been also studied, both in laminar and turbulent flow regimes. Pool boiling heat transfer of nanofluids is also being investigated. A detailed discussion about these results available in the literature can be found in Chapters 2 and 3. Very few studies have been conducted to investigate the flow boiling of nanofluids. Water is used as the base fluid in a number of studies investigating the heat transfer performance of nanofluids. Refrigerants have rarely been used as the base fluids due to their chemical nature and need of pressurized systems in the manufacturing process. Improvement in the refrigerant heat transfer due to use of nanofluids can lead to charge minimization and compact systems in air-conditioning and refrigeration applications.

1.3 Thermophysical properties

Properties of nanofluids like thermal conductivity and viscosity are of significance due to their impact on heat transfer and pressure drop in various applications. Measured properties of nanofluids relative to the base fluid can be useful to predict the thermal and hydraulic performance and thus can serve as screening criteria for nanofluids. Measurements of these properties for refrigerant-based nanofluids, however, present some challenges. First, to measure the properties of liquid refrigerants, instruments should work under pressurized conditions. The saturation pressures for R134a and CO$_2$ at 25°C are 0.66 and 6.43MPa, respectively. Second, the properties of these fluids can span over a broad range. For example, viscosity of CO$_2$ at 25°C is 0.06mPa-s, and viscosity of R134-based nanofluid is larger by at least three orders of magnitude. Thus, in order to measure thermal properties of refrigerant-based nanofluids, instruments must be carefully chosen based upon range, accuracy and the working conditions.
Thermal conductivity can be measured using a number of steady-state and transient techniques. In the transient hot wire technique, a line source of radial heat flux is used in stepwise time [3]. The heat source, which is required to lose heat only by conduction, is immersed in the fluid which is initially at an equilibrium state. The temperature rise in the fluid above its equilibrium value, in contact with the line source, can be predicted by the solution of the non-steady conduction equation. It is impossible not to introduce natural convection in measurement as the fluid adjacent to the heat source expands and develops buoyancy effects. However, with transient hot wire technique, measurements can be completed in a short time compared to the characteristic time required for these effects to influence the heat loss from the source and induce error in measurement. The technique developed for practical applications is also insensitive to the alignment and dimension of the cell in which the fluid is placed. An accurate mathematical model is in place to derive thermal conductivity from measurements made using transient hot wire. In addition, corrections necessary for this technique can all be implemented mathematically. Corrections are available to account for the finite dimensions of the wire, Knudsen effects due to use of thin wire, radiation effects, and variation in temperature dependent thermal properties. For measurements in electrically conducting fluids, wire with thin electrical insulation layer is used and the mathematical formulation of conduction equation is changed from that of a cylinder to a composite cylinder.

Viscosity of the fluid can be measured using a variety of instruments as well [3]. The advantages of a torsional quartz-crystal viscometer are that it can be used at extreme conditions such as low temperature and high pressures. It consists of a piezoelectric quartz crystal, optically polished and cut so that its electric axis coincides with its geometric axis. The crystal oscillates predominantly in a torsional mode. It is possible to measure the logarithmic decrease in torsional oscillations and viscosity of the fluid surrounding the crystal can be calculated by comparing this decrease to the similar decrease measured in vacuum. The oscillations, however, are electrically excited and the decrease can be also observed from the characteristics of the frequency response curve of the crystal near resonance. The later method of measurement is preferred due to better accuracy in measuring frequency. The viscometer is very compact due to small size of the crystal and can be used in extreme pressure and temperature conditions. The only connection it requires is the leads to the radio frequency bridge on the quartz crystal.
1.4 Two-phase flow

In a number of cooling applications, two-phase flows are favored over single-phase flows due to higher rate of heat removal and nearly constant temperature at which heat is removed. Single-phase flow can be completely analyzed by investigating inertial, viscous and pressure forces. In two-phase flow, in addition to these forces, interfacial tension forces, wetting behavior of the liquid on the surface, and liquid-vapor momentum exchange in the flow play an important role. Flow regimes in single-phase flow are primarily laminar, turbulent and transitional and are distinguished by Reynolds number, Re. In two-phase flow, the flow regimes are much more complex due to the interaction of liquid and vapor and are observed and recorded in reference to the mass flux, heat flux, quality and thermophysical properties. In horizontal flows, two-phase flow regimes are a little different than those in vertical flows due to the tendency for stratification. In horizontal flows at very low quality, bubbly flow is often observed. As the quality increases, small bubbles coalesce to form plug-type bubbles. Stratified flow is observed at a little higher qualities and low flow rates due to separation of vapor in the upper part of the tube. Further increase in quality and flow rate can introduce instabilities in the smooth liquid-vapor interface leading to wavy flow. At high flow rates, the waves span across the entire width of the tube forming large slug-type bubbles. Apart from these flow regimes, annular flows are also observed at high vapor velocities and moderate liquid flow rates. Finally, mist flows and dryout regions are observed at very high qualities in two-phase flow.

A number of models and flow regime maps are available in the literature to predict pressure drop and heat transfer during two-phase flow. A detailed description of these models and two-phase flow theory is readily available in textbooks [4-5]. Nucleate boiling is the dominant mechanism of evaporation at low qualities and near the onset of boiling. As more vapor is generated at high qualities, evaporation from liquid-vapor interface becomes more important. Further with the thinning of liquid film on the wall, film evaporation can become the dominant mechanism. At constant heat flux conditions, based upon the magnitude of the heat flux, the flow might be subjected to different heat transfer mechanisms. At low heat fluxes, subcooled nucleate boiling leads to saturated nucleate boiling, followed by convective boiling and dryout. At intermediate heat fluxes, subcooled nucleate boiling leads to saturated nucleate boiling, followed by saturated film boiling and mist evaporation. At very high heat fluxes, there is no nucleate boiling and subcooled film boiling leads to saturated film boiling and mist
evaporation. The onset of nucleate boiling is of interest in two-phase flows and marks the transition to combined convective and nucleate boiling. The onset depends on the fluid properties, imposed flow conditions and nucleation site distribution. The number of nucleation sites on a surface in turn depends on the thermal boundary layer thickness, subcooling, wall superheat and the thermophysical properties of the liquid, along with the properties of the solid surface. In most systems of practical interest, the onset of nucleate boiling is achieved at or just beyond the point where the bulk flow reaches the saturated liquid condition. At higher qualities, however, due to the development of the flow regimes, the forced convective boiling becomes stronger, suppressing the nucleate boiling effects. Thus to predict heat transfer coefficient in two-phase flow, an approach that accommodates transition from nucleate boiling mechanism to pure film evaporation is warranted. Most of the flow boiling models use some form of power law contribution of nucleate boiling and convective boiling contributions to evaluate two-phase heat transfer coefficients. These models almost invariably depend on empirical values from experimental investigation for use with different fluids.

1.5 Objectives of the study

Employing nanofluids to enhance heat transfer is attractive in a range of applications. It is confirmed with recent studies that the enhancements in thermal conductivity of nanofluids are within the bounds predicted by the classical theory, as opposed to anomalous enhancements reported in early experiments. However, even with relatively lower enhancements in thermal properties, the potential for enhancement in heat transfer applications is considerable. A few studies have shown enhancements in convective heat transfer using nanofluids. Enhancements in critical heat flux in pool boiling are apparently unanimous, and those in pool boiling heat transfer are debated. There is a lack of understanding of nanofluid physics due to limited experimental studies. Very few studies involving flow boiling of nanofluids have been reported in literature and only two experimental studies with flow boiling of refrigerant-based nanofluids are available to author’s knowledge. Refrigeration and air-conditioning industry has been working actively to reduce the use of refrigerants that are responsible for ozone depletion and global warming. Improved system efficiency could result in reduced energy usage, reduced global warming, and other favorable impacts on sustainability. Nanofluids with their superior thermal properties and
heat transfer performance can provide an attractive option. This creates a need to evaluate heat transfer performance of refrigerant-based nanofluids.

1.5.1 Novelty of the research

Experimental evaluation of the flow boiling heat transfer and pressure drop of refrigerant-based nanofluids is required to assess their potential in applications using such working fluids. Creation of these nanofluids at high pressures presents challenges that will be addressed in this study. The research will explore compatibility of different nanoparticles, surface-treated nanoparticles, and stabilizing agents with refrigerants to form stable dispersions. In addition to the commonly used refrigerant R134a, CO$_2$ will also be used as a base fluid. Due to its low global warming potential (GWP) and ozone depletion potential (ODP), CO$_2$ is considered a more environment-friendly refrigerant. Use of primary nanoparticle dispersion in compatible/miscible base oil will be evaluated for creation of stable dispersions in R134a and CO$_2$. Thermal conductivity and viscosity of refrigerant-based nanofluids will be measured. These data are not currently available in the literature. Further, heat transfer and pressure drop performance during flow boiling of refrigerant-based nanofluids will be evaluated to assess potential use of these fluids in application. It is also possible that parameters such as particle material, size, mass fraction, surface treatment, and base oil play significant role in thermal-hydraulic performance of refrigerant-based nanofluids. In this study, a systematic evaluation of the effects of aforementioned parameters will be undertaken, and recommendations for combinations for better thermal-hydraulic performance will be developed.

1.5.2 Statement of objectives

The objectives of this study include the following:

1. Create stable nanoparticle dispersions in R134a and CO$_2$. Investigate use of nanoparticles, surface treatments and refrigeration oil-based dispersions that are miscible in refrigerants.

2. Measure thermal conductivity and viscosity of refrigerant-based nanofluids. Evaluate effects of particle mass fraction on these properties.


1.6 Structure of the thesis

The rest of the thesis is organized as follows:

Chapter 2 presents experimental investigation of the flow boiling of CO₂-based nanofluids. A literature review on various topics such as use of CO₂ (R744) as refrigerant, thermal properties of nanofluids, convective heat transfer of nanofluids, pool and flow boiling heat transfer of nanofluids will be covered. Experimental apparatus and procedures will be introduced in experimental design section. Data reduction and baseline experimental data will be presented as well. Finally, experimental results on heat transfer and pressure drop during flow boiling of CO₂-based nanofluids will be presented along with synthesis and characterization of the nanofluids.

Chapter 3 presents experimental investigation of the flow boiling of R134a-based nanofluids. Literature review in this chapter will be slightly different from the one in chapter 2. The experimental apparatus, procedures and data reduction will be, however, similar to the one in chapter 2. This chapter will include thermal conductivity and viscosity measurements of R134a-based nanofluids. Finally, similar to chapter 2, this chapter will present experimental results on heat transfer during flow boiling of R134a-based nanofluids. The pressure drop data for the same nanofluids will not be included due to their low significance.

Chapter 4 will present the additional experimental results on pressure drop and subcooling of refrigerant-based nanofluids that have not been included in the manuscripts for journal publication. Chapter 5 will finally present detailed conclusions from this study and recommendations for future work.

Appendix A will present the data reduction code used in this study. Appendix B will contain visual images of the nanofluids and various components of the experimental apparatus that were not included in the manuscripts.
2.1 Overview

Nanofluids are expected to have better heat transfer performance, because their thermal properties are superior to those of the base fluid. Over the past decade a number of experiments to measure thermal properties and convective heat transfer coefficients of nanofluids have been reported. This study explores the use of nanofluids in flow boiling applications. Carbon dioxide (R744) was used as the base refrigerant. CuO nanoparticles, 40nm in size and TiO$_2$ nanoparticles, 200nm in size were dispersed in liquid carbon dioxide saturated at room temperature to create nanofluids. Experiments were conducted with each nanofluid to measure flow boiling heat transfer coefficients in a smooth copper tube, 6.23mm in diameter. Heat flux and mass flux were varied to cover a wide quality range and application conditions. CuO nanoparticles decreased the heat transfer performance by 5% during flow boiling while TiO$_2$/CO$_2$ nanofluid exhibited an average decrease of 28% in heat transfer coefficients. Pressure drop in the smooth copper tube during flow boiling was also measured for two nanofluids and did not show significant change from the baseline. Deterioration of flow boiling heat transfer may largely be due to the deposition of nanoparticles on the surface, filling up micro-cavities that provide nucleating sites in the nucleate boiling dominated flow. Other parameters such as particle size, surface treatment, and mass fraction may be important as well, and generalizations of improved heat transfer performance with nanofluids should be scrutinized.

2.2 Literature review

Almost a century after its initial use as a refrigerant, carbon dioxide is gaining serious consideration for refrigeration applications, due to its non-toxicity, non-flammability, zero ODP and very low GWP [6]. It is proving to be an attractive option for low-temperature applications in cascade systems [7] and transcritical systems with suitable modifications [8]. Bansal [9] provided a detailed review of the current status of CO$_2$ as a refrigerant. The favorable properties of CO$_2$, such as low surface tension, low viscosity, low ratio of liquid to vapor density, low specific volume, and steep vapor-pressure curve are often cited as advantageous when compared to other refrigerants. An average flow boiling heat transfer coefficient ratio for R22:R134a:CO$_2$ was reported to be 1:0.8:2 by Choi et al. [10]. High volumetric refrigeration capacity along with
high pressure rating makes microchannel or minichannel heat exchangers ideal for CO\textsubscript{2} refrigeration systems. Flow boiling of CO\textsubscript{2} in microchannels and minichannels has been studied by a few researchers [10-14]. Pettersen [13] used a heated glass tube to visualize and construct a two-phase flow pattern map. Annular and intermittent flow regimes were dominant in visualization and nucleate boiling dominated heat transfer at low/medium vapor fractions. A flow-regime-based model for CO\textsubscript{2} evaporation inside smooth tubes was proposed by Cheng et al. [15-16]. The model was shown to be applicable to a wide range of tube diameter, heat flux, mass flux and saturation temperature. Over 1000 data points were used to validate the model, and it was shown to predict 71\% of the data within ±30\%. All the studies that provided the data points either used stainless steel or aluminum test sections. The flow-regime-based model was originally developed for R134a, R123, R402A, R404A and R502 [17-19] and was modified for dryout and mist flow conditions in CO\textsubscript{2}. The new model was then verified for flow regimes with data from Gasche [11] obtained using a rectangular channel, 0.8mm in hydraulic diameter. Mastrullo et al. [20] commented on disagreement in the literature between the heat transfer data for CO\textsubscript{2} at similar operating conditions. They also studied flow boiling heat transfer of CO\textsubscript{2} in a 6mm diameter stainless steel tube at operating conditions matching those in dry-expansion evaporators. Ono et al. [21] conducted experiments to study flow pattern, heat transfer and pressure drop during flow boiling of pure CO\textsubscript{2} and CO\textsubscript{2}-oil mixtures. The flow patterns observed in a 3.76mm diameter smooth tube were different from those proposed by Cheng et al. [15]. Oh and Son also studied flow boiling heat transfer and pressure drop of CO\textsubscript{2}. They found the heat transfer results to be in agreement with the prediction by Cheng et al. [15]; however, the pressure drop results did not match predictions from any existing empirical correlations.

Recent advances in nanotechnology have opened up new possibilities in various fields of engineering, including fluid dynamics and heat transfer. Nanofluids are stable dispersions of nanoparticles in a base fluid. The particle size generally ranges from 1 to 100nm. Enhancement in thermal properties is one of the significant reasons cited for superior performance of nanofluids. Thermal conductivity enhancements of various nanofluids are widely reported in literature. Apart from favorable thermal properties, nanofluids are also expected to exhibit better heat transfer performance due to nucleation on particle surfaces, and surface modifications due to nanoparticle deposition. The classical approach to predict thermal conductivity of non-interacting spherical particles dispersed in a fluid was outlined by Maxwell using effective
A number of modifications to this prediction method have been proposed, one of which accounted for different shapes of particles and interfacial thermal resistance known as Kaptiza resistance [23]. Early experimental studies reported much higher enhancements in thermal conductivity of nanofluids than those predicted by classical theory [24]. Most of these early experiments were documented in a review article by Yu et al. [25]. Recent analysis of classical bounds and careful measurements with verifiable standards has shown conductivity enhancements to be within the limits of classical theory [26-27]. It should be noted that 36 different organizations across the world participated in a study by Buongiorno et al. [26] to verify thermal conductivity of four sets of nanofluids using different measurement techniques. While thermal conductivity of nanofluids has received the maximum attention, reported measurements on properties such as viscosity and specific heat are following suit. Mahbubul et al. [28] wrote a review article concerning the latest developments on viscosity measurements of nanofluids. According to the review, viscosity trends with respect to particle material, size, and mass fraction were contradictory in different reports. There was also disagreement as to whether nanofluids were Newtonian or non-Newtonian fluids. While an increase in viscosity with particle mass fraction was commonly reported, the trend of increase was not agreed upon. Mahbubul and co-workers concluded that there was a need for more reliable and standardized data to understand viscosity behavior of nanofluids. Specific heat of nanofluids has not received much attention and a study by Wang et al. reported a decrease in it with increasing particle mass fraction [29]. Nanofluid properties vary with stability of the fluid and degree of agglomeration in dispersion which may account for disagreement between reported thermophysical properties in literature [30]. A few methods and instrumentation to measure relative stability of nanofluids were outlined in a review by Ghadimi et al. [31].

Experimental results for convective heat transfer of nanofluids were tabulated with their enhancement ratios in a review by Yu et al. [25]. In the review, heat transfer enhancements exceeding the thermal conductivity enhancements were quite often reported and attributed to particle-fluid interactions. In laminar flow, an increase in the Reynolds number, Re, increased the enhancement ratio of the Nusselt number for particle volume fractions over 2%. For lower particle concentrations, effect of Re was significant. An increase in particle mass fraction increased the enhancement ratios in most cases, while the particle size and particle material had minor influences. In turbulent flow, data were limited and showed heat transfer enhancements
independent of $Re$. An increase in enhancement was observed with increase in particle mass fraction. A review of convective heat transfer correlations proposed for nanofluids was provided by Sarkar [32]. According to the review, some of the existing correlations were modified to account for the enhancements exceeding those due to thermal conductivity. Apart from many experimentally based correlations, the review also reported correlations based on numerical and analytical approaches. The analytical approach was outlined by Buongiorno [33] and identified Brownian diffusion and thermophoresis as the two most important nanoparticle/base-fluid slip mechanisms. Nanoparticle diffusion effects in the boundary layer near the wall seemed to play a significant role and the enhancements were explained using reduction of viscosity in the boundary layer and consequent thinning of laminar sublayer. In the review by Sarkar [32], pressure drop data of nanofluids closely matched with the predictions from conventional correlations for base fluid in both laminar and turbulent flow conditions. A need for more reliable experimental data for convective heat transfer of nanofluids was evident from the review.

Boiling of nanofluids has been a topic of interest in recent years. A review by Barber et al. [34] outlined most of the experimental results in pool boiling and flow boiling. A majority of the experiments used water as the base fluid. Water, due to its polar nature, is a promising base fluid. Untreated nanoparticles have shown better dispersion stability in water than in hydrocarbons, HFCs and HCFCs [35]. In the review by Barber et al., experiments on the effects of nanoparticles on boiling heat transfer coefficient ($h$) and critical heat flux (CHF) were mainly reported. Enhancements in CHF were unanimously observed. Deposition of nanoparticles on the heater surface was reported to be one of the main reasons for CHF enhancements [36-38]. Kim et al. [38] showed that the deposition of nanoparticles improved surface wettability by measuring reduced contact angle on the surface. This improved wettability helped rewetting of hot spots on the heating surface, thus, improving CHF. Kim et al. [39] showed that CHF was similar for nanofluid boiling on a clean surface and base fluid boiling on nanoparticle-fouled surface. Further corroboration of increased wettability of nanoparticle-coated surface was exhibited through contact angle measurements. A slightly different explanation of nanoparticles improving the stability of evaporating microlayer on the surface was suggested for improvement in CHF. Unlike CHF, enhancements in $h$ were debated. The review by Barber et al. listed 22 experimental studies out of which 10 showed enhancement, 8 showed deterioration and 4
showed no change in $h$ with the use of nanofluids. Deterioration in $h$ was widely attributed to the deposition of nanoparticles filling up micro-cavities on surface resulting in reduction of nucleation sites. The enhancement in $h$ was thought to be due to nanoparticle interaction with bubbles and improved thermal conductivity at the heater surface. The nucleation site density, bubble departure diameter and bubble frequency were all expected to be affected by nanoparticles. Stability of nanofluids has not been very well documented in many reports but was expected to play a significant role in boiling of nanofluids as it does in thermophysical properties. Likewise, the use of surfactants and surface treatments on the particles used to improve nanofluid stability has not been well documented. Barber et al. concluded that pre-coating a heater surface with nanoparticles can be advantageous over boiling with nanofluids. Reports on boiling heat transfer of refrigerant-based nanofluids are limited. A review by Cheng and Liu [40] provided 16 reports (from 6 different groups) in pool boiling and 5 reports (from 2 different groups) in flow boiling of refrigerant-based nanofluids. In pool boiling, CNT increased $h$ in R123 and R134a [41], TiO$_2$ nanoparticles decreased $h$ in R141b [42], CuO nanoparticles increased $h$ in R113 [43]. Kedzierski [44] reported that CuO nanoparticles enhanced $h$ in POE/R134a mixture by as much as 275%. It was observed that the enhancements decreased with increasing lubricant mass fraction. Apart from improved thermal conductivity which appeared to be responsible for 20% of the enhancement, secondary nucleation and particle mixing were the possible reasons cited for additional improvement. Kedzierski also reported that Al$_2$O$_3$ nanoparticles provided the most favorable enhancements with the largest lubricant mass fraction tested in Al$_2$O$_3$/POE/R134a nanofluid [45]. The mass fraction of Al$_2$O$_3$ in POE was fixed at 5.6%. The average heat flux improvement over the baseline for same degree of wall superheat was approximately 105, 49 and 155% for 0.5, 1 and 2% lubricant mass fraction in R134a, respectively. The momentum transfer from nanoparticles to the bubbles was assumed to be responsible for the enhancement. Peng et al. [46] reported enhancements as high as 63% in pool boiling of oil/R113 mixture. Enhancements improved with increases in nanoparticle mass fraction in nanoparticle/oil dispersion and decreased with increases in nanoparticle/oil dispersion mass fraction in R113. Similar behavior was reported by the same authors for CNT and Cu nanoparticles. It should be noted that while the literature in pool boiling of other nanofluids is evenly divided over the enhancements in $h$, all but one study [42] reported enhancements in refrigerant-based nanofluids. However, 10 out of 16 studies showing enhancements were
reported by the same group of authors, and corroboration of the results by other groups would be useful.

Only two reports are available in the literature addressing flow boiling of refrigerant-based nanofluids [35, 47]. The other reports tabulated in the review by Cheng and Liu are either parts of those reports or conference proceedings that eventually led to those reports. Peng et al. [47] studied flow boiling of CuO/R113 nanofluid in a copper tube, 9.5mm in diameter and 1.5m in length. R113 was used as the base fluid because it is in liquid state at room temperature and atmospheric pressure, aiding in dispersion of nanoparticles. The average diameter of CuO nanoparticles was 40nm. Flow boiling heat transfer coefficients, $h$, showed an increase of up to 30% with the use of nanofluids. Reduction in the boundary layer and formation of molecular adsorption layer on the surface of nanoparticles were reported as possible reasons for enhancement. Henderson et al. [35] conducted flow boiling experiments with R134a and POE/R134a base fluids in a smooth copper tube, 7.9mm in diameter and 2m in length. For SiO$_2$/R134a nanofluid, 0.5 and 0.05% in volume fraction, a decrease in $h$ of up to 55% was observed. Deterioration in $h$ was more pronounced at higher particle mass fractions. For CuO/POE/R134a nanofluid, no significant change in $h$ was observed for 0.02% volume fraction, but average enhancements of 52 and 76% were observed for 0.04 and 0.08% volume fractions, respectively. The enhancement in $h$ was shown to remain with the use of base fluid after cleaning the apparatus, indicating surface modification as a possible cause. Inability of SiO$_2$ nanoparticles to achieve similar results was attributed to their hydrophobic coating. It is important to note that the baseline data for experiments showing enhancements were quite low in magnitude (0.4 - 0.9kW/m$^2$K) for $h$ during flow boiling of R134a. The highest average vapor quality used in these experiments was 7.3%.

It is evident from the above discussion that no experimental data for the flow boiling of CO$_2$-based nanofluids are currently available in the literature. Such data can add to a relatively small set of existing experimental results on the flow boiling of nanofluids and can advance our understanding of the relevant physics; moreover, these data will allow engineers to assess the impact of nanoparticles on CO$_2$ refrigeration systems, which are of emerging technical importance. This work also addresses the unique challenges in creating nanofluids at very high pressures. A number of readily available nanoparticles, surface-treated particles and stabilizing
agents are explored to form stable dispersions in CO$_2$. An alternative technique using nanoparticles dispersed in base oils compatible/miscible with CO$_2$ is also explored.

2.3 Experiment design

2.3.1 Apparatus

A pressure vessel constructed of SS 316Ti alloy (Berghof Inc.) was used to create and verify stability of refrigerant-based nanofluids. The pressure vessel was 3.08 liters in volume and designed for maximum pressure of 15MPa. The temperature range was -30 to 150°C. The vessel was equipped with two borosilicate glass windows, 30mm in diameter and opposite to each other, for visual inspection of nanofluids. A magnetic stirrer (0-2000rpm) with two sets of paddle wheels was installed at the center of the vessel for continuous stirring of nanofluids. A heating/cooling coil was used to control the temperature, and PTFE insulation was used to reduce heat transfer with surroundings. The vessel was also equipped with rupture disc, pressure sensor, pressure gauge, thermocouple well, liquid extraction valves, and vapor extraction valves.

A closed recirculating loop was used to measure $h$ during flow boiling of nanofluids. The nanofluid was circulated using a GC series gear pump with M25 gear set (Micropump Inc.) coupled with a 0.33HP TENV motor (Baldor Inc.). A VS1ST series variable frequency drive, VFD (Baldor Inc.) was used to control motor rpm, thus controlling the mass flow rate of nanofluid in the loop. A Coriolis-effect flow sensor (ELITE series, Micro Motion Inc.) was used along with a 2700 series transmitter to measure the mass flow rate and density. The test section was constructed of smooth copper tube, 6.23mm in diameter and 1.8m in length. Thermocouples were attached at seven different axial locations on the test section, dividing it in six sub-sections, each 250mm in length. The sub-sections were centered on the test section. Two thermocouples, one at the top and the other at the bottom, were placed at each of the seven cross sections. Thermocouple beads were attached to the surface of the tube into small slots using thermal epoxy. The slots were 1 x 0.5 x 0.5mm in dimension. Two Omegalux rope heaters (Omega Inc.), 5mm in diameter and 3.05m in length, were used as heat source for the test section. Each rope heater was rated at 500W with 240V input. Power input to the rope heaters was supplied using N5771A dc power supply (Agilent technologies) rated at 1500W. The test section along with heat source was used as an evaporator in the closed loop. A configuration similar to that of test section was used as a preheating section upstream of the test section. No surface thermocouples
were attached to the preheating section. A B17 brazed plate heat exchanger (SWEP Inc.) with ten plates was used as a condenser in the loop. The maximum working pressure of the condenser was 14MPa. The condenser exchanged heat with an ethylene glycol/water solution supplied by a laboratory chiller system. A turbine flow meter and transmitter (Flow Technology Inc.) were used to measure the mass flow rate of the glycol solution. Sheath thermocouples were used to measure fluid temperatures in the chiller loop at the inlet and exit of the condenser. A sample cylinder (Swagelok), one liter in internal volume, was used as a receiver in the closed loop. The flow circulated from the exit of the pump, through flow sensor, preheating section, test section, condenser, receiver, and then returned to the pump. The temperature of the fluid was measured using sheath thermocouples at the inlet and exit of the preheating section, inlet and exit of the test section, inlet and exit of the condenser, and exit of the receiver. The absolute pressure in the system was measured at the inlet and exit of the test section and that of the condenser. A bypass was used between the exit of the pump and the inlet of the receiver and was controlled using a needle valve when very low mass flow rates were needed in the closed loop. A schematic of the recirculating loop along with the flow direction is provided in Figure 2.1. Data from flow sensors, dc power sources, pressure transducers, and thermocouples were recorded using current and voltage cDAQ modules (National Instruments).

2.3.2 Procedure

A technique commonly known as two-step approach for nanofluid preparation is as follows: obtain/create nanoparticles/nanolubricant and then disperse it into a base fluid. The technique is easy to implement in comparison to the one-step approach, in which nanoparticles are created and simultaneously dispersed in the base fluid. The two-step approach was adopted in the current work. The mass of the nanoparticles/nanolubricant was measured using a mass balance. The known quantity of nanoparticles was placed inside the pressure vessel. The pressure vessel was closed and evacuated. The mass of the nanoparticles was measured before and after the evacuation process in one case to confirm no significant loss of nanoparticles during evacuation. The vessel was then charged with a known quantity of CO₂ from a pressurized tank. Chilled water at 5°C was circulated through the heating/cooling coil to help condense CO₂ in the vessel. The mixture of nanoparticles and liquid CO₂ (saturated at room temperature) was then
stirred using magnetic stirrer at 800rpm for about 3 hours. Stability of nanofluids was visually inspected through the sight glass over a period of about one week.

The required amount of nanofluid was transferred to the flow boiling apparatus using a transfer vessel. Pressure in the flow boiling apparatus was lowered using chilled water supply to the condenser. Heat transfer experiments were conducted at varying mass flux and heat flux values. Mass flux and heat flux were controlled using the frequency input to the gear pump unit and the voltage input to the dc power supply, respectively. The saturation pressure was slightly different for each combination of mass flux and heat flux. The system was allowed to achieve steady state by observing recorded variables with time. Variables like mass flow rate, voltage and current from dc power supply, surface temperatures, fluid temperatures, and absolute pressures in the system were recorded using a LabVIEW program and data acquisition system. A single measurement point was obtained by averaging 100 readings over a period of 7 minutes.

2.4 Experimental approach

2.4.1 Data analysis

The thermophysical properties of pure CO₂ were evaluated using Engineering Equation Solver (EES). The enthalpies of pure CO₂ were used for CO₂-based nanofluids due to the low particle mass fraction (≈ 0.1%). The fluid was always subcooled at the test section inlet. The enthalpy at the test section inlet was evaluated using measured temperature and pressure. Because the rope heaters were uniformly wound around the test section, the energy input was assumed to be uniform throughout the test section. The enthalpy at each thermocouple station on the test section was evaluated using

\[ i_n = i_{in} + \left( \frac{L_n}{L} \right) \frac{Q}{m_{ref}} \]  

(2.1)

where subscript \( n \) denotes the station number on test section, \( i_{in} \) is the enthalpy at the inlet of the test section, \( L_n \) is the distance between the inlet and \( n^{th} \) station on the test section, \( L \) is the total length of the test section, \( Q \) is the total heat input from the heaters, and \( m_{ref} \) is the mass flow rate of the refrigerant. Due to seven thermocouple stations, the test section was divided into six sub-sections. The vapor quality and saturation temperature in each sub-section were evaluated using
averaged values of enthalpy and pressure. The saturation temperature was used as refrigerant temperature when the vapor quality was between 0 and 1. Experiments were conducted in increments of heat flux values. The mass flux was varied at each heat flux to vary vapor quality in sub-sections. The maximum quality change (at combination of highest heat flux and lowest mass flux) in a sub-section was limited to 20%. The heat flux was evaluated using

\[ q = \frac{Q}{2\pi r_1 L} \]  

(2.2)

where \( r_1 \) is the inner radius of the tube. A heat balance within ±5% was verified for \( Q \) in ancillary experiments, using a single-phase flow in the test section. The averaged flow boiling heat transfer coefficients in each sub-section were evaluated using

\[ h = \frac{k q}{k(T_w - T_{ref}) - q r_1 \ln((r_o - 0.0005)/r_1)} \]  

(2.3)

where \( k \) is the thermal conductivity of the tube wall, \( T_w \) is the wall temperature averaged from four thermocouple readings on each sub-section, \( T_{ref} \) is the refrigerant temperature, and \( r_o \) is the outer radius of the tube. Depth of the thermocouple slot, 0.0005m, is subtracted from \( r_o \) to account for the modified outer radius of the test section. In addition to \( h \), pressure drop in the test section was measured and cast in terms of pressure drop per unit length using

\[ \Delta P/L = \frac{P_{in} - P_{exit}}{L} \]  

(2.4)

where \( P_{in} \) and \( P_{exit} \) are absolute pressures at the inlet and exit of the test section, respectively.

2.4.2 R134a baseline data

Comparison of experimental \( h \) during flow boiling of R134a was done with correlations available in the literature and is shown in Figure 2.2. Slope of the experimental data agreed with the predictions of Shah [48]; however, the magnitudes were underpredicted. The data showed better agreement with the model of Kattan and co-workers [17], both in slope as well as in
magnitude. Based on the comparison, 71% of the experimental data were within ±30% of the predictions by the model of Kattan and co-workers. With exclusion of data at the lowest heat flux (5kW/m²) and lowest mass flux (110kg/m²s), 91% of the data (199/218 data points) were within ±30% of the predictions. The general agreement of the experimental data with models available in literature was encouraging for the use of the flow boiling apparatus for further experiments.

2.4.3 Experimental conditions

A comparison of all the results from nanofluids was conducted with the baseline data from pure CO₂. Experimental conditions and uncertainties for nanofluid and baseline data are tabulated in Table 2.1 and Table 2.2, respectively.

2.5 Results from CO₂-based nanofluids

Nanofluids were created using the aforementioned procedure. Two nanoparticles, CuO and TiO₂, were successfully dispersed in CO₂ and used for nanofluid experiments in this study. A list of all the nanoparticles that were tested for dispersion stability in liquid CO₂ is provided with their respective manufacturer in Table 2.3. The mass fraction of nanoparticles was subject to change during transfer from pressure vessel to flow boiling apparatus using transfer vessel as well as due to deposition on the surface of flow boiling apparatus. So, the mass fraction of the nanofluid was also measured after flow boiling experiments using sensitive mass measurements.

2.5.1 CuO/CO₂ nanofluid

CuO nanoparticles, 40nm in size were used to create a CO₂-based nanofluid. Nanoparticles were provided by United Technologies Research Center (UTRC) and were coated with fluoropolymer for better dispersion in liquid CO₂. Nanoparticles, 5.1g in mass, were added to 3.4kg of CO₂ to create nanofluid. The total mass of nanofluid transferred to the flow boiling apparatus was 2.66kg. A comparison of \( h \) during flow boiling of CuO/CO₂ nanofluid in a smooth copper tube to that of pure CO₂ under similar experimental conditions is shown in Figure 2.3a. For CuO/CO₂ nanofluid, 91% of the flow boiling \( h \) data were within ±20% of the baseline while 71% of the data were within ±10% of the baseline. The result exhibits noticeable change in \( h \) due to use of CuO nanoparticles. An average decrease of 5% was observed in \( h \) with CuO/CO₂
nanofluid. Further, pressure drop during nanofluid flow in 1.8m long test section was measured and compared with that from pure CO₂. As shown in Figure 2.3b, the pressure drop per unit length was not affected by the presence of CuO nanoparticles under these conditions.

The mass fraction of CuO nanoparticles in the nanofluid was measured after completion of heat transfer experiments using mass balance measurements. A weighed sample of nanofluid from the flow boiling apparatus was allowed to slowly bleed CO₂ vapor. A needle valve with very small opening was used for bleeding at an approximate rate of 20g/hour for 15 hours. The mass of nanoparticles was measured with an accurate balance after complete evaporation of CO₂ from nanofluid. An average particle mass fraction of CuO/CO₂ nanofluid was measured to be 0.09% using three samples. The initial mass fraction during preparation of CuO/CO₂ nanofluid was 0.15%. Based upon the amount of nanofluid transferred to the flow boiling apparatus, it is expected that approximately 1.6g of nanoparticles were trapped inside the closed loop. Most of these nanoparticles are expected to coat the inner surface of the apparatus including that of the test section. No surface analysis of the test section was conducted but the test section was cleaned by circulating acetone multiple times in the closed loop. Residue of nanoparticles was evident in the acetone used for cleaning purpose in the first batch.

2.5.2 TiO₂/CO₂ nanofluid

TiO₂ nanoparticles with an average size of 200nm were also used to create a stable nanofluid for the study. The particles were manufactured by Phosphorex Inc. and coated with an undisclosed proprietary surface treatment. Nanoparticles, 9.8g in mass, were mixed with 3.64kg of CO₂ to create nanofluid. The total mass of nanofluid transferred to the flow boiling apparatus was 2.72kg. Comparison of h for TiO₂/CO₂ nanofluid to that for pure CO₂ is shown in Figure 2.4a. A significant decrease in h was observed with the use of TiO₂ nanoparticles. Comparison of pressure drop per unit length is shown Figure 2.4b. Similar to CuO nanoparticles, no significant change in pressure drop was observed due to use of TiO₂ nanoparticles.

The decrease in h during flow boiling of TiO₂/CO₂ nanofluid was as high as 60%. An average value of decrease using 401 data points was found to be 28%. The decrease in h was higher for mass flux values smaller than 400kg/m²s. An average decrease of 34% (306 data points) and 8% (95 data points) was observed for mass flux values smaller and larger than 400kg/m²s, respectively. Variation of percentage change in h (%h) with mass flux at the largest
heat flux (25kW/m²) used in the experiment is shown in Figure 2.5a. At G = 380kg/m²s, %h was -20% and increased to +6% at G = 440kg/m²s. The two data points were measured in the same sub-section of the test section. The change in vapor quality between the two points was from 0.23 to 0.19. Similar abrupt increase in %h was seen at all heat flux values except at the lowest heat flux (5kW/m²) where smooth increase in %h was observed and is shown in Figure 2.5b. Experimental conditions of the data from Figure 2.5a are plotted on a flow pattern map of CO₂ based on the model by Cheng et al. [15] in Figure 2.6a. The data points plotted from left to right in Figure 2.6a are the experimental conditions of points plotted in Figure 2.5a from right to left. It can be concluded from Figure 2.6a that the abrupt increase in %h is due to change in the flow regime from annular to intermittent. However, the physical parameters that may be responsible for decrease in %h in annular flow are highly probable in intermittent flow as well. Addition of nanoparticles affects thermophysical properties of the base fluid. Flow regime boundaries are quite sensitive to some of these properties such as liquid density and surface tension. The thermophysical properties of nanofluids were not measured in the current study. Available models in literature that include dependence of thermophysical parameters on flow regime boundaries use modified empirical constants to curve fit experimental data for different refrigerants; thus, they may not precisely reflect the effects of modified properties. It is likely that the addition of nanoparticles might delay the transition from stratified-wavy to annular flow from 200kg/m²s for pure CO₂ to 400kg/m²s for TiO₂/CO₂ nanofluid. The result of the hypothesis is depicted in Figure 2.6b with modified flow boiling map for TiO₂/CO₂ nanofluid. According to the modified map, %h is drastically improved when the flow is transitioned from stratified wavy to intermittent flow regime. The heat transfer mechanism is quite different in stratified wavy and intermittent flow and better fits the result of sudden increase in %h.

During flow boiling, the onset of nucleate boiling is expected to occur at or above a certain heat flux, \( q_{ONB} \), which can be calculated using surface tension, saturation temperature, convective heat transfer coefficient, enthalpy of evaporation, and vapor density [49]. For the experimental conditions in this study, \( q_{ONB} \) was always less than 1kW/m². Low value of \( q_{ONB} \) for CO₂ compared to R22 and R134a can be attributed to its high liquid to vapor thermal conductivity ratio, low liquid to vapor viscosity ratio, and lower surface tension. In additions, CO₂ also has much lower liquid to vapor density ratio leading to lower vapor velocities in two phase flow. These factors are responsible for nucleate boiling dominated heat transfer during
flow boiling of CO$_2$ [50]. The heat flux range of 5 to 25kW/m$^2$ used in the current study further ensures that nucleate boiling was the dominant mechanism during flow boiling of nanofluids. It is possible that at moderate qualities in stratified-wavy flow, nucleate boiling is suppressed due to presence of nanoparticles. Changes in surface roughness systematically affecting nucleate boiling of nanofluids have been reported in literature [51-52]. Das et al. [51] reported considerable reduction in the surface roughness of cylindrical cartridge heater after pool boiling with water. The surface returned to its original condition on cleaning with water jet. The size of the nanoparticles used in the experiment (20-50nm) were an order of magnitude smaller than surface roughness (0.2-1.2µm) making their entrapment in micro-cavities easy. As micro-cavities constitute majority of nucleation sites during pool boiling, measured decrease in nucleate boiling was justified. In the current study, surface roughness of smooth copper tube is expected to be in the range from 1-2µm. TiO$_2$ nanoparticles were 200nm in size. A similar physical mechanism reducing nucleation sites during nucleate-boiling-dominated flow can cause decrease in $h$ as observed with TiO$_2$/CO$_2$ nanofluid. However, at lower qualities in intermittent flow regime, enough nucleation sites are generated to match heat transfer performance of pure CO$_2$. It should be noted that the heat flux range used in the two reports [35, 47] that showed enhancements in flow boiling using nanofluids is lower than their respective $q_{ONB}$.

Precise mass balance measurements were used to measure mass fraction of nanofluid after heat transfer experiments. An average mass fraction of TiO$_2$/CO$_2$ nanofluid was found to be 0.05% using measurements from two samples. The initial mass fraction of TiO$_2$/CO$_2$ nanofluid during its preparation was 0.27%. Based upon the amount of nanofluid transferred to the flow boiling apparatus, 5.9g of TiO$_2$ nanoparticles were trapped inside the closed loop, providing surface coating to the test section and rest of the apparatus. The mass of TiO$_2$ nanoparticles trapped inside flow boiling apparatus is approximately three and a half times larger than that of CuO nanoparticles. This may explain no apparent change in heat transfer performance during flow boiling of CuO/CO$_2$ nanofluid as opposed to significant decrease in $h$ for TiO$_2$/CO$_2$ nanofluid. Thermal conductivity of CuO and TiO$_2$ nanoparticles is reported to be 20 and 12W/m-K, respectively. These values are quite close to each other as compared to the thermal conductivity of liquid CO$_2$ saturated at 10°C, 0.1W/m-K. This indicates that the effect of nanofluids on heat transfer performance during flow boiling is mostly limited to surface modification. Particle size, 200nm for TiO$_2$ and 40nm for CuO nanoparticles, may also play a
significant role in suppression of nucleate boiling. The critical radius of 300nm is recommended for nucleate boiling based upon flow boiling data in commercial tubing [49]. In addition, effect of surface treatment of nanoparticles may play a role in nucleate boiling of nanofluids.

2.5.3 Baseline data after use of nanofluid
The flow boiling apparatus was cleaned by circulating acetone after completion of nanofluid experiments. Baseline experiments with pure CO\(_2\) were then repeated to check for any modification in heat transfer owing to the surface modification due to nanofluids. Comparison of \(h\) of baseline 2 (after use of nanofluids) with baseline 1 (before use of nanofluids) is shown in Figure 2.7a. Good agreement was found between the two experiments; 94% of data from baseline 2 were within ±20% of those from baseline 1. The result indicates that there is no permanent surface modification in the test section due to use of nanofluids at least from heat transfer perspective. This result is similar to the findings of Das \textit{et al.} [51] in which modified surface roughness returned to its original condition on cleaning with water jet. It also validates cleaning procedure of flow boiling apparatus using acetone and further use of the test section for experiments with other nanofluids. Data for pressure drop per unit length in the test section from the two baselines were also compared and are shown in Figure 2.7b.

2.6 Conclusions
CO\(_2\)-based nanofluids were created and tested for heat transfer performance in flow boiling experiments. Following conclusions were drawn from the study:

- CuO/CO\(_2\) nanofluid did not show any significant change in \(h\) during flow boiling. TiO\(_2\)/CO\(_2\) nanofluid showed significant decrease in \(h\) during flow boiling compared to its baseline. An average decrease of 28% was observed in \(h\). The deterioration in \(h\) was dependent on mass flux and showed marked improvement at mass fluxes above 400kg/m\(^2\)s. Pressure drop in the test section was unchanged with the use of nanofluids.
- Nucleate boiling was the dominant mechanism of heat transfer during all experimental conditions. In TiO\(_2\)/CO\(_2\) nanofluid, it was conjectured that nanoparticles suppressed nucleate boiling at moderate qualities and showed deterioration in heat transfer performance. Modification to the existing flow regime map was proposed that limited
decrease in $h$ to stratified-wavy flow and no significant change in $h$ during intermittent flow regime.

- Decrease in $h$ during flow boiling of TiO$_2$/CO$_2$ nanofluid may be due to filling up of micro-cavities owing to the deposition of nanoparticles on the test surface. This can be corroborated with reduction in the mass fraction of nanoparticles after flow boiling experiments. The decrease in mass fraction of CuO nanoparticles was much smaller than that of TiO$_2$ nanoparticles in their respective nanofluids.

- Nanofluids can significantly decrease heat transfer performance in evaporators. This result may not be general but specific to the size and surface treatment of TiO$_2$ nanoparticles used in this study. This is quite likely true for optimistic flow boiling results of nanofluids in literature. Generalized heat transfer performance results of nanofluids must be accepted and used with caution unless effect of multiple parameters such as particle, particle size, surface treatment, mass fraction and base fluid are systematically reported.

- Liquid CO$_2$ is not an ideal base fluid for dispersing nanoparticles. A more systematic approach using surface treatments to improve dispersibility of nanoparticles in CO$_2$ is needed to make stable nanofluids. A fluoropolymer coating was found successful in partially dispersing CuO nanoparticles in CO$_2$. Surface treated (Phosphorex Inc. proprietary) TiO$_2$ nanoparticles also dispersed partially in CO$_2$. 
2.7 Figures and Tables

Figure 2.1: Schematic of the flow boiling apparatus.
Figure 2.2: Comparison of flow boiling heat transfer coefficients of R134a with models available in literature.
Figure 2.3: Comparison of a) $h$ and b) pressure drop in smooth copper tube for CuO/CO$_2$ nanofluid with baseline.
Figure 2.4: Comparison of a) $h$ and b) pressure drop in smooth copper tube for TiO$_2$/CO$_2$ nanofluid with baseline.
Figure 2.5: Variation in \% change in $h$ for TiO$_2$/CO$_2$ nanofluid with mass flux at a) $q = 25\text{kHz/m}^2$ and b) $q = 5\text{kHz/m}^2$. 
Figure 2.6: Experimental conditions for data points from figure 2.5a represented on a) flow regime map by Cheng et al. and b) modified flow regime map. Data points from left to right correspond to those in figure 2.5a from right to left.
Figure 2.7: Comparison of a) $h$ and b) pressure drop in smooth copper tube after the use of nanofluids with baseline.
Table 2.1: Experimental conditions for flow boiling of nanofluids

<table>
<thead>
<tr>
<th>Variable</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat flux</td>
<td>5 to 25 kW/m²</td>
</tr>
<tr>
<td>Mass flux</td>
<td>100 to 1000 kg/m²/s</td>
</tr>
<tr>
<td>Quality</td>
<td>0 to 1</td>
</tr>
<tr>
<td>Saturation temperature</td>
<td>9 to 12°C</td>
</tr>
</tbody>
</table>

Table 2.2: Experimental uncertainty in recorded variables during flow boiling of nanofluids

<table>
<thead>
<tr>
<th>Variable</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>± 0.1°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>± 1 kPa</td>
</tr>
<tr>
<td>Mass flow rate</td>
<td>± 0.1%</td>
</tr>
<tr>
<td>Energy balance</td>
<td>± 5%</td>
</tr>
<tr>
<td>Heat transfer coefficients</td>
<td>± 10%</td>
</tr>
</tbody>
</table>

Table 2.3: List of nanoparticles/dispersions tested for dispersion stability in CO₂

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Particles/Dispersions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sun Innovations</td>
<td>SiO₂, Al₂O₃, SiO₂ (oil treated), MWCN</td>
</tr>
<tr>
<td>Phosphorex</td>
<td>TiO₂ (proprietary surface treated)</td>
</tr>
<tr>
<td>NanoArc</td>
<td>Fe₂O₃</td>
</tr>
<tr>
<td>NanoTek</td>
<td>ZnO (non-polar), ZnO (polar)</td>
</tr>
<tr>
<td>UTRC</td>
<td>TiO₂, Graphite, CuO (fluoropolymer coated), MWCN (COOH functionalized)</td>
</tr>
<tr>
<td>Sigma Alderich</td>
<td>Ti/mineral oil</td>
</tr>
<tr>
<td>MKNano</td>
<td>Ag, Cu/mineral oil</td>
</tr>
<tr>
<td>Nanophase</td>
<td>Al₂O₃/RL22H, ZnO/RL22H, Al₂O₃/RL68H, CuO/RL68H (all POE oil dispersions)</td>
</tr>
</tbody>
</table>
CHAPTER 3: R134a-BASED NANOFLOUIDS

3.1 Overview

The thermal properties and flow boiling heat transfer coefficients of R134a-based nanofluids were measured. Stable nanofluids were created in R134a by mixing it with dispersions of surface-treated nanoparticles in polyolester (POE) oil (RL22H and RL68H). The particles (Al$_2$O$_3$, ZnO, CuO, and ATO) at particle mass fractions from 0.08% to 1.34%, with particle sizes of 20nm and 40nm were coated with polar and non-polar surface treatments. Thermal conductivity showed limited improvements; the highest increase of 13% was observed with CuO nanoparticles. Significant increases in viscosity were observed, as high as 2147% due to CuO nanoparticles. Only the ATO nanofluid showed a decrease in the measured viscosity. Heat transfer coefficients during flow boiling of nanofluids were measured over a range of mass flux from 100 to 1000 kg/m$^2$s, with a heat flux from 5 to 25kW/m$^2$, and vapor quality up to 1. The test section was a smooth copper tube, 6.23mm in diameter and 1.8m in length. Average decreases in heat transfer during flow boiling at the highest particle mass fraction were 15% and 22% for Al$_2$O$_3$ and ZnO nanoparticles, respectively. CuO nanoparticles exhibited an average decrease of 7% for particle mass fraction of 0.08%. An average increase of 10% was observed with ATO nanoparticles at a 0.22% mass fraction. Heat transfer performance deteriorated with increase in viscosity and particle number density. The performance was also worse for partially stable nanofluids that modified the test section surface. Modifications to the thermophysical properties was the primary mechanism that affected heat transfer performance during flow boiling of nanofluids; increased thermal conductivity enhanced while increased viscosity and surface tension reduced heat transfer in nucleate boiling dominated flows. A secondary mechanism of nanoparticles filling up the micro-cavities on the test surface was also responsible for decreased heat transfer and was a strong function of particle number density.

3.2 Literature review

Nanofluids are stable dispersions of nanoparticles in a base fluid. The particle size generally ranges from 1 to 100nm. Nanofluids have shown to exhibit superior heat transfer performance as a consequence of enhanced thermal properties and a few other proposed mechanisms such as nucleation on particle surfaces, and surface modifications due to
nanoparticle deposition. Thermal conductivity enhancements of nanofluids are widely reported in literature. The classical approach to predict thermal conductivity of non-interacting spherical particles dispersed in a fluid was outlined by Maxwell using the effective medium theory [22]. Modifications to this prediction method have been proposed, one of which accounted for different shapes of particles and interfacial thermal resistance known as Kaptiza resistance [23]. Early experimental studies reported much higher enhancements in thermal conductivity of nanofluids than those predicted by classical theory [24]. Most of these early experiments were documented in a review article by Yu et al. [25]. Recent analysis of classical bounds and careful measurements with verifiable standards has shown conductivity enhancements to be within the limits of classical theory [26-27]. The study by Buongiorno et al. [26] involved collaborative efforts from 36 different organizations to verify thermal conductivity of nanofluids using different measurement techniques. Viscosity of nanofluids has received some attention in recent years. Mahbubul et al. [28] wrote a review article addressing the latest developments on viscosity measurements of nanofluids. According to the review, viscosity trends with respect to particle material, size, and mass fraction were contradictory in different reports. Both Newtonian and non-Newtonian behavior was observed for different nanofluids. While an increase in viscosity with particle mass fraction was commonly reported, the trend of increase was not agreed upon. A need for more reliable and standardized data to understand viscosity behavior of nanofluids was evident. Specific heat of nanofluids has not received much attention and a study by Wang et al. [29] reported decrease in it with increasing particle mass fraction. Nanofluid properties were found to vary with stability of the fluid and degree of agglomeration in dispersion which may account for disagreement between reported thermophysical properties in literature [30]. A few methods and instrumentation techniques to measure relative stability of nanofluids were outlined in a review by Ghadimi et al. [31].

A number of review articles addressing performance of nanofluids in single-phase flow are available in open literature [25, 32, 53-57]. Most of these review articles have tabulated results for modifications to the forced convective heat transfer and pressure drop due to nanofluids. While a few early reviews concluded that the heat transfer enhancements exceeded the enhancements in thermal conductivity [25, 56], more recent ones indicated thermophysical properties to be the dominant mechanism for convective heat transfer improvement in nanofluids [53]. Instead of comparing Nusselt number at constant Reynolds number, Yu et al. [53]
formulated figure of merit ratios that combined changes in heat transfer coefficients and pumping power due to nanofluids. Enhancements in heat transfer coefficients, $h$, were then compared against figure of merit ratios based upon constant flow velocity and constant pumping power. Nanofluid $h$ for turbulent flow were quite accurately predicted by standard single-phase flow correlations like Dittus-Boelter, Petukhov-Popov, and Gnielinski. Reviews also show lack of agreement between experimental results from different authors, often poor performance of nanofluids, lack of understanding of physical mechanisms, and variation in nanofluid preparation process. Systematic modification of thermal conductivity and viscosity of nanofluids to enhance heat transfer and minimize pressure drop penalty was suggested by adjusting a variety of controllable parameters. A review of convective heat transfer correlations proposed for nanofluids was provided by Sarkar [32]. According to the review, some of the existing correlations were modified to account for the enhancements exceeding those due to thermal conductivity. Apart from many experimentally based correlations, the review also reported correlations based on numerical and analytical approaches. The analytical approach was outlined by Buongiorno [33] and identified Brownian diffusion and thermophoresis as the two most important nanoparticle/base-fluid slip mechanisms. Nanoparticle diffusion effects in the boundary layer near the wall seemed to play a significant role and the enhancements were explained using decrease in viscosity in the boundary layer and consequent thinning of the laminar sublayer. In the review by Sarkar [32], pressure drop data of nanofluids closely matched with the predictions from conventional correlations for base fluid in both laminar and turbulent flow conditions.

Boiling of nanofluids has been a topic of interest in recent years. Junhong et al. [58] showed that the use of water-based magnetic nanofluids enhanced $h$ during pool boiling, even in the absence of a magnetic field; the enhancement showed further improvement when a magnetic field was applied. Water, due to its polar nature, is a promising base fluid. Untreated nanoparticles have shown better dispersion stability in water than in hydrocarbons, HFCs and HCFCs [35]. A review by Barber et al. [34] outlined most of the experimental results in pool boiling and flow boiling. Enhancements in critical heat flux, CHF were unanimously observed while those in $h$ were debated. The review listed 22 experimental studies out of which 10 showed enhancement, 8 showed deterioration and 4 showed no change in $h$ with the use of nanofluids. Deposition of nanoparticles on the heater surface leading to increased wettability and improved
stability of evaporating microlayer were reported as main reasons for CHF enhancement while enhancement in $h$ was attributed to the nanoparticle interaction with bubbles and improved thermal conductivity at the heater surface. Deterioration in $h$ was associated with the nanoparticles filling up micro-cavities on the surface resulting in reduction of nucleation sites.

For refrigerant-based nanofluids, Cheng and Liu [40] reviewed 16 reports (from 6 different groups) in pool boiling and 5 reports (from 2 different groups) in flow boiling. Park and Jung [41] reported enhancement in nucleate pool boiling with addition of carbon nanotubes (CNT) in R123 and R134a. Enhancement in $h$ as high as 36% was observed at heat fluxes less than 30kW/m$^2$. Trisaksri and Wongwises [42] investigated nucleate boiling of TiO$_2$ nanoparticles dispersed in R141b and found decrease in $h$ with increase in particle volume fraction. Peng et al. [43] found increase in $h$ up to 55% with CuO nanoparticles dispersed in R113. Nanofluids were also manufactured by dispersing nanoparticles in refrigerant-oil mixture. Kedzierski and Gong [44] reported that CuO nanoparticles enhanced $h$ in RL68H/R134a mixture by as much as 275%. They also observed that the enhancement decreased with increasing lubricant mass fraction. Apart from improved thermal conductivity which appeared to be responsible for 20% of the enhancement, secondary nucleation and particle mixing were the possible reasons cited for additional improvement. In a separate study, Kedzierski [45] reported that Al$_2$O$_3$ nanoparticles provided the most favorable enhancements with the largest lubricant mass fraction tested in Al$_2$O$_3$/RL68H/R134a nanofluid. The mass fraction of Al$_2$O$_3$ in RL68H was fixed at 5.6%. The average heat flux improvement over the baseline for the same degree of wall superheat was approximately 105, 49, and 155% for 0.5, 1, and 2% lubricant mass fraction in R134a, respectively. The momentum transfer from nanoparticles to the bubbles was assumed to be responsible for the enhancement. Peng et al. [46] reported enhancements in $h$ as high as 63% during pool boiling by dispersing diamond nanoparticles in VG68/R113 mixture. Enhancements improved with increases in nanoparticle mass fraction in nanoparticle/oil dispersions and decreased with increases in nanoparticles/oil dispersion mass fraction in R113. Similar behavior was reported by the same authors for CNT and Cu nanoparticles dispersed in VG68/R113 mixture. It should be noted that while the literature on pool boiling of other nanofluids is evenly divided over the enhancements in $h$, all but one study [42] reported enhancements in refrigerant-based nanofluids. However, 10 out of 16 studies showing enhancements were reported by the same group of authors, and corroboration of the results by other groups would be useful.
Only two reports are available in the literature addressing flow boiling of refrigerant-based nanofluids [35, 47]. The other reports tabulated in the review by Cheng and Liu are either parts of those reports or conference proceedings that eventually led to those reports. Peng et al. [47] studied flow boiling of CuO/R113 nanofluid in a copper tube, 9.5mm in diameter and 1.5m in length. R113 was used as the base fluid because it is in the liquid state at room temperature and atmospheric pressure, aiding in dispersion of nanoparticles. The average diameter of the CuO nanoparticles was 40nm. An increase of up to 30% was observed in $h$ with the use of nanofluids during flow boiling. Reduction in the boundary layer and formation of molecular adsorption layer on the surface of nanoparticles were reported as possible reasons for enhancement. Henderson et al. [35] conducted flow boiling experiments with R134a and POE/R134a base fluids in a smooth copper tube, 7.9mm in diameter and 2m in length. For SiO$_2$/R134a nanofluid, 0.5 and 0.05% in volume fraction, decreases in $h$ of up to 55% were observed. The deterioration in $h$ was more pronounced at higher particle mass fractions. For CuO/POE/R134a nanofluid, no significant change in $h$ was observed for 0.02% volume fraction, but average enhancements of 52 and 76% were observed for 0.04 and 0.08% volume fractions, respectively. The enhancements in $h$ were shown to remain with the use of base fluid after cleaning the apparatus, indicating surface modification as a possible cause. The inability to achieve similar results with SiO$_2$ nanoparticles was attributed to their hydrophobic coating. It is important to note that the baseline data for experiments showing enhancements were quite low in magnitude (0.4 - 0.9kW/m$^2$K) for $h$ during flow boiling of R134a. The highest average vapor quality used in these experiments was 7.3%.

R134a is one of the commonly used refrigerants in the contemporary refrigeration industry. A study to investigate flow boiling heat transfer of R134a-based nanofluids will provide possible opportunities to improve efficiency, compactness and charge requirement of a number of commercial systems. It will also provide a benchmark for improvement in other refrigerants like R1234yf and R1234ze that are poised to replace R134a in the near future. Effects of various parameters like particle material, size, mass fraction, surface treatment, and base oil have not been investigated in the limited studies on flow boiling of nanofluids available in the literature. The current work by studying these parameters will present more comprehensive understanding of the flow boiling of refrigerant-based nanofluids. This will help understand
physical mechanisms introduced due to nanoparticles during flow boiling and lead researchers a step closer to their successful applications in the refrigeration industry.

3.3 Experiment design

3.3.1 Apparatus

A pressure vessel constructed of SS316Ti alloy (Berghof Inc.) was used to create and measure thermal properties of refrigerant-based nanofluids. The pressure vessel was 3.08 liters in internal volume and designed for maximum pressure of 15MPa. The temperature range was -30 to 150°C. The vessel was equipped with two borosilicate glass windows, 30mm in diameter and opposite to each other, for visual inspection of nanofluids. A magnetic stirrer (0-2000rpm) with two sets of paddle wheels was installed at the center of the vessel for continuous stirring of nanofluid. A heating/cooling coil was used to control the temperature, and PTFE insulation was used to reduce heat transfer with surroundings. Thermal conductivity of nanofluids was measured using a sensor from F5 Technologies. The sensor employed transient hot wire measurement technique [59-60] using a 100μm platinum hot wire. It was custom designed to measure thermal conductivity in low viscosity fluids like R134a by lowering the energy input to avoid convective effects. A quartz viscometer (F5 Technologies) was used to measure dynamic viscosity of nanofluids. The viscometer utilized principle of suppression of torsional vibrations in the quartz element [61]. Both sensors were able to operate in the temperature and pressure ranges from -30 to 150°C and 0 to 7MPa, respectively. The sensors were mounted on the pressure vessel using ISO threads and EPDM o-rings. The vessel was also equipped with rupture disc, pressure sensor, pressure gauge, thermocouple well, liquid extraction valves, and vapor extraction valves.

A closed recirculating loop was used to measure $h$ during flow boiling of nanofluids. The nanofluid was circulated using a GC series gear pump with M25 gear set (Micropump Inc.) coupled with a 0.33HP TENV motor (Baldor Inc.). A VS1ST series variable frequency drive, VFD (Baldor Inc.) was used to control motor rpm, thus controlling the mass flow rate of nanofluid in the loop. A Coriolis-effect flow sensor (ELITE series, Micro Motion Inc.) was used along with a 2700 series transmitter to measure the mass flow rate and density. The test section was constructed of smooth copper tube, 6.23mm in diameter and 1.8m in length. Thermocouples
were attached at seven different axial locations on the test section, dividing it in six sub-sections, each 250mm in length. The sub-sections were centered on the test section. Two thermocouples, one at the top and the other at the bottom, were placed at each of the seven cross sections. Thermocouple beads were attached to the surface of the tube into small slots using thermal epoxy. The slots were 1 x 0.5 x 0.5mm in dimension. Two Omegalux rope heaters (Omega Inc.), 5mm in diameter and 3.05m in length, were used as heat source for the test section. Each rope heater was rated at 500W with 240V voltage input. Power input to the rope heaters was supplied using N5771A dc power supply (Agilent technologies) rated at 1500W. The test section along with heat source was used as an evaporator in the closed loop. A configuration similar to that of the test section was used as preheating section upstream of the test section. No surface thermocouples were attached to the preheating section. A B17 brazed plate heat exchanger (SWEP Inc.) with ten plates was used as a condenser in the loop. The maximum working pressure of the condenser was 14MPa. The condenser exchanged heat with an ethylene glycol/water solution supplied by a laboratory chiller system. A turbine flow meter and transmitter (Flow Technology Inc.) were used to measure the mass flow rate of the glycol solution. Sheath thermocouples were used to measure fluid temperatures in the chiller loop at the inlet and exit of the condenser. A sample cylinder (Swagelok), one liter in internal volume, was used as a receiver in the closed loop. The flow circulated from the exit of the pump, through flow sensor, preheating section, test section, condenser, receiver, and then returned to the pump. The temperature of the fluid was measured using sheath thermocouples at the inlet and exit of the preheating section, inlet and exit of the test section, inlet and exit of the condenser, and exit of the receiver. The absolute pressure in the system was measured at the inlet and exit of the test section and that of the condenser. A bypass was used between the exit of the pump and the inlet of the receiver and was controlled using a needle valve when very low mass flow rates were needed in the closed loop. A schematic of the recirculating loop along with the flow direction is provided in Figure 3.1. Data from flow sensors, dc power sources, pressure transducers, and thermocouples were recorded using current and voltage cDAQ modules (National Instruments).

3.3.2 Procedure

All R134a-based nanofluids used in this study were created using polyolester (POE) oil dispersions supplied by Nanophase Inc. POE oils, RL22H and RL68H, were selected to create
dispersions because they have good miscibility in R134a and are commonly used in various industrial applications. Five different surface treatments, all Nanophase proprietary, were applied on Al₂O₃ nanoparticles to create stable dispersions in RL22H. These dispersions were checked for stability in R134a using pressure vessel apparatus. One out of five surface treatments yielded very stable R134a-based nanofluid and was used thereafter to create nanofluids using different nanoparticles. The stability of nanofluid was evident on visual inspection through sight windows of pressure vessel. The successful surface treatment yielded stable nanofluid without any stirring while other surface treatments did not yield stable nanofluid even after hours of stirring. The successful surface treatment was visually observed in stagnant condition without stirring for one week and did not show any visible agglomeration or settlement of particles. Very little residue of nanoparticles was obtained from the pressure vessel during cleaning process after removal of the stable nanofluid. Images of one such stable nanofluid and its constituent nanoparticles are shown in Figure 3.2.

As no stirring was needed to create R134a-based nanofluids, nanofluids were created in a reservoir that could be easily connected and disconnected from closed recirculation loop. The reservoir was 3.75 liters in internal volume and was equipped with a rupture disc. A known quantity of oil dispersion was transferred to the reservoir and then the latter was evacuated using a vacuum pump. A known mass of R134a was charged to the reservoir to create nanofluid and the latter was then connected to the flow boiling apparatus using a ball valve. The flow boiling apparatus was also evacuated before allowing nanofluid to transfer from reservoir. Pressure in the flow boiling apparatus was controlled using chilled water supply to the condenser and the total mass of nanofluid transferred from the reservoir. Heat transfer experiments were conducted at varying mass flux and heat flux values. Mass flux and heat flux were controlled using the frequency input to the gear pump unit and the voltage input to the dc power supply, respectively. The saturation pressure was slightly different for each combination of mass flux and heat flux. The system was allowed to achieve steady state by observing recorded variables with time. Variables like mass flow rate, voltage and current from dc power supply, surface temperatures, fluid temperatures, and absolute pressures in the system were recorded using a LabVIEW program and data acquisition system. A single measurement point was obtained by averaging 100 readings over a period of 7 minutes.
3.3.3 Data analysis

The saturation state and enthalpy of baseline oil/R134a mixtures and nanofluids were needed for data reduction. Data obtained using Engineering Equation Solver (EES) for pure R134a were used instead as the presence of oil (2% mass fraction) and nanoparticles (< 1.4% mass fraction) was not considered significant enough to affect the reduced variables beyond their uncertainty. The assumption was confirmed for oil/R134a mixtures using statistical thermodynamic modeling in one study [62]. Properties such as thermal conductivity and viscosity that are known to be affected due to the presence of oil and nanoparticles were measured in this study. However, these properties were not required for the data reduction. The fluid was always subcooled at the test section inlet. The enthalpy at the test section inlet was evaluated using measured temperature and pressure. Because the rope heaters were uniformly wound around the test section, the energy input was assumed to be uniform throughout the test section. The enthalpy at each thermocouple station on the test section was evaluated using

\[ i_n = i_{in} + \left( \frac{L_n}{L} \right) \frac{Q}{m_{ref}} \]  

(3.1)

where subscript \( n \) denotes the station number on test section, \( i_{in} \) is the enthalpy at the inlet of the test section, \( L_n \) is the distance between the inlet and \( n^{th} \) station on the test section, \( L \) is the total length of the test section, \( Q \) is the total heat input from the heaters, and \( m_{ref} \) is the mass flow rate of the refrigerant. Due to the use of seven thermocouple stations, the test section was divided into six sub-sections. The vapor quality and saturation temperature in each sub-section were evaluated using averaged values of enthalpy and pressure. The saturation temperature was used as refrigerant temperature when the vapor quality was in between 0 and 1. Experiments were conducted in increments of heat flux values. The mass flux was varied at each heat flux to vary vapor quality in sub-sections. The maximum quality change (at combination of highest heat flux and lowest mass flux) in a sub-section was limited to 20%. The heat flux was evaluated using

\[ q = \frac{Q}{2\pi r_1 L} \]  

(3.2)
where \( r_i \) is the inner radius of the tube. A heat balance within ±5% was verified for \( Q \) in ancillary experiments, using a single-phase flow in the test section. The averaged flow boiling heat transfer coefficients in each sub-section were evaluated using

\[
h = \frac{kq}{k(T_w - T_{ref}) - qr \ln((r_o - 0.0005)/r_i)}
\]  

(3.3)

where \( k \) is the thermal conductivity of the tube wall, \( T_w \) is the wall temperature averaged from four thermocouple readings on each sub-section, \( T_{ref} \) is the refrigerant temperature, and \( r_o \) is the outer radius of the tube. Depth of the thermocouple slot, 0.0005m, is subtracted from \( r_o \) to account for the modified outer radius of the test section. In addition to \( h \), pressure drop in the test section was measured and cast in terms of pressure drop per unit length using

\[
\Delta P/L = \frac{P_{in} - P_{exit}}{L}
\]  

(3.4)

where \( P_{in} \) and \( P_{exit} \) are absolute pressures at the inlet and exit of the test section, respectively.

3.3.4 Experimental conditions

Comparison of all the results from nanofluids was done with the baseline data from oil/R134a mixtures. Experimental conditions and uncertainties are tabulated in Table 3.1 and Table 3.2, respectively. Using combination of 5 different heat fluxes, 18 different mass fluxes and multiple qualities, approximately 450 to 500 measurements were made during each baseline and nanofluid experiment. Majority of these measurements were recorded at low qualities. In each experiment, approximately 78% of the measurements were made at qualities below 0.2, 21% were made between qualities of 0.2 and 0.7, and only 1% were made at qualities higher than 0.7.

3.4 Thermophysical properties of nanofluids

Measured thermal properties of all the fluids are tabulated in Table 3.3. As mentioned earlier, temperature \( (T) \), thermal conductivity \( (k) \), and dynamic viscosity \( (\mu) \) were measured. Measurement ranges on the viscosity and conductivity sensors were 0.1 to 500mPa-s and 0 to 2W/m-K, respectively. Properties of water and R134a were measured before measurements of
nanofluids and showed reasonable agreement with the values from EES. The viscosity sensor was not very accurate in the range below 1mPa-s as evident from the measurement of R134a that showed 33% deviation from the value available in EES. Viscosity of water, however, was measured with only 6% error from the value available in EES. Measurement uncertainty for viscosity accounting for repeatability of measurements and reproducibility of the instrument was 2%. The sensor was not calibrated for very low viscosity range as viscosity of nanofluids due to the presence of POE oils and nanoparticles was expected to be much higher than 1mPa-s and the measurement accuracy was sacrificed for the wider measurement range. Thermal conductivity of R134a also showed 10% error from the value available in EES. The accuracy in measurement of $k$ was also sensitive to the viscosity of fluid as it was easy for convection effects to creep in the measurements at low viscosity. Thermal conductivity of water, however, exactly matched the value available in EES due to higher viscosity of water. The measurement uncertainty for $k$ was 1%. Similar to viscosity sensor, the conductivity sensor was not calibrated for very low viscosity fluids. For POE oils, RL22H and RL68H, measured $\mu$ and $k$ were in the right ranges. Viscosity of these oils at higher temperatures, 40 and 100°C, were available in the literature.

The effect of nanoparticles on thermal properties of POE oil was observed using $\text{Al}_2\text{O}_3$/RL22H dispersion with particle mass fraction of 40%. Thermal conductivity showed an increase of 65% while increase in viscosity was 621% due to the presence of nanoparticles. It is interesting to note that for the same mass fraction, increase in $\mu$ was about 10 times larger than the increase in $k$. The effect of POE oil on thermal properties of R134a was observed using RL22H/R134a and RL68H/R134a mixtures. These mixtures with similar mass fractions of oils were used to obtain the baseline data for heat transfer experiments with nanofluids. Thermal conductivity exhibited small apparent decrease due to the presence of oil in R134a. The decreases in $k$ were 2% and 1.8% due to RL22H and RL68H, respectively. However the decreases were observed in comparison with erroneous measurements of pure R134a. In comparison with the value from EES, $k$ showed an increase of 11% and 10% due to 2% mass fraction of RL22H and RL68H, respectively. The slightly higher increase in $k$ due to RL22H compared to RL68H is expected as measured $k$ for RL22H is higher than RL68H. Viscosity, on the other hand, increased significantly due to the presence of POE oils. Increases of 339 and 400% in $\mu$ were observed due to RL22H and RL68H oils, respectively. The respective increases were 515 and 600% in comparison with the viscosity values of pure R134a in EES. Thermophysical
properties of nanofluids were compared with properties of oil/R134a mixtures. These measured properties of baseline mixtures were more accurate due to their higher viscosity as evident from the measurements in water and R134a.

Variation in thermal properties with particle mass fraction was observed using 20nm Al$_2$O$_3$/RL22H/R134a nanofluid. Mass fraction of POE oil in all the nanofluids was 2%. Small enhancements were observed in $k$ and increased approximately linearly with increases in particle mass fraction. Improvements in $k$ of 1, 1.4, and 2.3% were observed at the particle mass fractions of 0.23, 0.55, and 1.41%, respectively. The viscosity increased due to the nanoparticles; however, the increase was not linear with particle mass fraction. The increases in the viscosity were 310, 529, and 436% for the particle mass fractions of 0.23, 0.55, and 1.41%, respectively. Similar viscosity trends of nanofluids that attain peak values with increases in particle mass fraction were found in literature [63].

Variation in thermal properties was also observed with different nanoparticles in RL22H/R134a mixtures. At the highest mass fraction of nanoparticles used in this study (1.4%), increases in thermal conductivity of 2.3, 2, 3.1, and 3.9% and increases in viscosity of 436, 298, 312, and 381% were observed due to 20nm Al$_2$O$_3$, 40nm Al$_2$O$_3$, 20nm ZnO, and 40nm ZnO nanoparticles, respectively. The 20nm particle size exhibited higher increases in both $k$ and $\mu$ compared to 40nm particle size for Al$_2$O$_3$ nanofluid while it was the other way around for ZnO nanofluids. The trend of commensurate increase in $k$ and $\mu$ was also observed with nanofluids created using RL68H/R134a mixture. An increase of 0.7% in $k$ and 203% in $\mu$ was observed for Al$_2$O$_3$/RL68H/R134a nanofluid, 0.53% in particle mass fraction. These increases were only half of those observed in Al$_2$O$_3$/RL22H/R134a nanofluid of similar mass fraction. The highest increase in both $k$ and $\mu$ were observed in CuO/RL68H/R134a nanofluid, 0.24% in particle mass fraction; increase in $k$ was 13% while that in $\mu$ was 2147%. For ATO/RL68H/R134a nanofluid with particle mass fraction of 0.25%, a small increase of 0.3% was observed in $k$ while a decrease of 22% was observed in $\mu$. ATO nanofluid was the only nanofluid that exhibited a decrease in viscosity.

3.5 Baseline experiments

Comparison of experimental $h$ during flow boiling of R134a was done with correlations available in the literature and is shown in Figure 3.3. Slope of the experimental data agreed with
the predictions of Shah [48]; however, the magnitudes were under-predicted. The data showed better agreement with the model of Kattan and co-workers [17], both in slope as well as in magnitude. Based on the comparison, 71% of experimental data were within ±30% of the predictions of Kattan and co-workers. With exclusion of data at lowest heat flux (5kW/m²) and lowest mass flux (110kg/m²s), 91% of the data (199/218 measurements) were within ±30% of the predictions. The ballpark agreement of the experimental data with models available in literature was encouraging for the use of flow boiling apparatus for further experiments.

Baseline data for comparison with results from R134a-based nanofluids were obtained with RL22H/R134a and RL68H/R134a mixtures. The oil mass fraction in the baseline mixtures as well as in all the nanofluids was fixed at 2%. Comparison of $h$ during flow boiling of RL22H/R134a mixture against pure R134a at similar experimental conditions is shown in Figure 3.4a. Increases in $h$ for oil mixture were observed. To systematically analyze the data, ratios of the two heat transfer coefficients were plotted against quality in Figure 3.4b. It can be seen that the ratios are larger than 1 for lower qualities and decrease to values lower than 1 for qualities higher than 0.7. A similar trend was observed for ratios of $h$ with RL68H/R134a mixture to that with pure R134a at similar conditions and is shown in Figure 3.5a. This behavior is in line with the data available in the literature for RL68H/R134a mixture [64] and is expected due to augmentation in the nucleate boiling with the presence of oil at low and intermediate qualities. Presence of oil is expected to promote foaming at the boiling surface which in turn can modify normal bubble growth and departure [65]. Other parameters that are significantly affected due to presence of oil are viscosity, surface tension and contact angle. The nucleate boiling contribution is not as significant compared to the convective boiling contribution at qualities over 0.7. In addition, the local oil concentration is high at higher qualities. And even though the chances of dryout are reduced due to presence of an oil film, the temperature of the bulk oil rises towards wall temperature decreasing the potential for heat transfer. In addition, the viscosity of the oil/refrigerant mixture is high at higher qualities due to higher mass fraction of oil. So, a slight decrease is observed in $h$ at higher qualities. Experimental heat transfer coefficients for RL22H/R134a mixture were not available in the literature.

While both oil/R134a mixtures exhibit increased heat transfer performance over pure R134a during flow boiling at low and intermediate qualities, enhancements in RL68H/R134a mixture were lower than those in RL22H/R134a mixture. This is evident from comparison of $h$
from the two mixtures in Figure 3.5b. An average decrease of 7% was observed in $h$ for RL68H/R134a compared to RL22H/R134a. Furthermore, the decrease was more pronounced at lower heat fluxes. Decreases in $h$ were 12.3, 9.1, 5.8, 4.9, and 3.2% for heat fluxes of 5, 10, 15, 20, and 25kW/m$^2$, respectively. RL22H had a manufacturer-reported viscosity of 105SUS (21.7mPa-s) compared to the RL68H viscosity of 300SUS (64.6mPa-s) at 100°F (37.8°C). The measured viscosities at 25°C were 53 and 245mPa-s for RL22H and RL68H, respectively. However, the viscosity difference between the 2% mass fraction of oil/R134a mixtures was only 13.8%, 1.23mPa-s for RL22H/R134a and 1.4mPa-s for RL68H/R134a. So, while heat transfer performance improved due to the presence of oil at low and moderate qualities in both oil/R134a mixtures, it decreased due to a small increase in viscosity.

Increase in viscosity can lead to decrease in convective boiling contribution similar to single-phase convective heat transfer. Bandarra and co-workers [66] argued that in two-phase flow, $h$ is shown to be directly proportional to the single phase liquid heat transfer in almost all prediction methods and single-phase heat transfer decreases with increase in viscosity for fully developed turbulent flow. This can be observed from the Dittus-Boelter equation to predict single-phase $h$ in turbulent flows:

$$h = \frac{k}{d} 0.023 \left( \frac{\rho V d}{\mu} \right)^{0.8} \left( \frac{\mu c_p}{k} \right)^{0.4}$$  \hspace{1cm} (3.5)

where $d$ is the tube diameter, $\rho$ is the fluid density, $V$ is the fluid velocity, and $c_p$ is the specific heat of the fluid. Equation 3.5 can be reduced as below:

$$h \propto \left( \frac{1}{\mu} \right)^{0.4}$$  \hspace{1cm} (3.6)

Equation 3.6 indicates that an increase in $\mu$ leads to a decrease in single-phase $h$ in turbulent flows. Equations similar to the form used in equation 3.5 are often used to predict $h$ during forced convective boiling and have similar dependence on $\mu$. One such equation used in the literature [17] is as follows:
where $\delta$ is the liquid film thickness in two-phase flow. Equation 3.7 can be reduced as below:

$$h \propto \left( \frac{1}{\mu} \right)^{0.29}$$  \hspace{1cm} (3.8)

Equation 3.8 also shows inverse proportionality of $\mu$ on convective boiling $h$. Heat transfer during nucleate boiling is also a function of fluid properties. A correlation to predict dependence of applied heat flux, $q$, on temperature difference, $\Delta T$, during nucleate pool boiling was formulated by Rohsenow [67]:

$$q = \mu_f i_{fg} \left[ \frac{g(\rho_f - \rho_g)}{\sigma} \right]^{0.5} \left( \frac{c_{p,f} \Delta T}{C_{S,f} i_{fg} Pr^n_f} \right)^3$$ \hspace{1cm} (3.9)

where subscripts $f$, $g$ and $fg$ denote liquid, vapor and liquid to vapor conditions, respectively. $g$ is the acceleration due to gravity, $\sigma$ is the surface tension of the fluid, $Pr$ is the Prandtl number of the fluid, $C_{S,f}$ is a constant based upon surface-liquid combination, $n$ is a constant based on fluid (1 for water and 1.7 for other fluids). Equation 3.9 can be used to obtain $h$ during nucleate boiling and further investigate its dependence on $\mu$ as follows:

$$h = \mu_f i_{fg} \left[ \frac{g(\rho_f - \rho_g)}{\sigma} \right]^{0.5} \left( \frac{c_{p,f} \Delta T}{C_{S,f} i_{fg} Pr^n_f} \right)^3 \Delta T^2$$ \hspace{1cm} (3.10)

$$h \propto \left( \frac{1}{\mu} \right)^2$$ \hspace{1cm} (3.11)

Equation 3.11 indicates decrease in $h$ during nucleate boiling due to increase in $\mu$. Another correlation to predict nucleate pool boiling $h$ can be obtained from Forster and Zuber [68] and its dependence on viscosity can be evaluated as follows:

$$h = 0.00122 \left( \frac{k_f^{0.79} c_{p,f}^{0.45} \rho_f^{0.49}}{\sigma^{0.5} i_{fg}^{0.24} \mu_f^{0.29} \rho_g^{0.24}} \right) \Delta T_{sat}^{0.24} \Delta P_{sat}^{0.75}$$ \hspace{1cm} (3.12)
The above analysis of convective and nucleate boiling heat transfer correlations indicates that an increase in viscosity is detrimental for heat transfer performance during flow boiling.

Apart from viscosity, another important fluid property that drastically affects boiling heat transfer is surface tension. Increased viscosity in oil/R134a mixtures was observed to be accompanied with increase in surface tension for small mass fractions of POE Solest 120 lubricant [69]. Empirical correlations between surface tension and viscosity for saturated liquids including R134a are available in literature [70] and can be used to predict increase in surface tension with viscosity at current experimental conditions. The correlation for pure R134a over-predicts the magnitude of surface tension for oil/R134a mixture by as much as 50%. The increased surface tension, however, plays a direct role in nucleation, bubble growth and departure, and the onset of nucleate boiling. This can justify decreased \( h \) for more viscous oil/R134a mixture and close comparison in \( h \) at high heat flux conditions.

Effect of oil on heat transfer during flow boiling of refrigerants is still an active area of research. However, most of the studies are concerned with the effect of oil mass fraction. The effect of two different oil/R134a mixtures on heat transfer and pressure drop during flow boiling in smooth and enhanced tubes was studied by Eckels and co-workers [71]. They used ester lubricants, 169 and 369SUS in viscosity. They found that the 169SUS oil increased \( h \) by 10% at oil mass fraction of 1.9% in smooth tubes. At higher oil mass fraction of 5%, \( h \) decreased by 25%. For 369SUS oil, however, continuous decrease was observed with increase in oil mass fraction. The average decrease was 28% at the oil mass fraction of 5%. The effect of oil on flow boiling of oil/refrigerant mixtures may depend on a number of parameters like miscibility, foaming, nucleation, thermophysical properties, and flow regimes. However, it is evident from the literature as well as current experimental data that POE oils enhanced \( h \) during flow boiling at low and moderate qualities and the enhancements decreased with increase in viscosity. A few other studies exhibiting adverse effects of viscosity on nucleate boiling of various fluids due to suppression of convection in the boundary layer, and suppression of bubble formation and growth were also found in the literature [72-75].
3.6 Results from R134a-based nanofluids

Flow boiling heat transfer experiments of R134a-based nanofluids were conducted using different nanoparticles, particle sizes, particle mass fractions, and base oils. The nanoparticles that were used in the study were alumina (Al$_2$O$_3$), zinc oxide (ZnO), copper oxide (CuO), and antimony tin oxide (ATO). An approximate mean diameter of 20nm was used for all the nanoparticles and the particle size distribution was lognormal. An additional particle size of 40nm was used in case of Al$_2$O$_3$ and ZnO nanoparticles. Four different particle mass fractions were studied in case of 20nm Al$_2$O$_3$ nanofluid; 0.08, 0.22, 0.50, and 1.34%. Particle mass fractions of 0.08 and 0.22% were also explored in case of CuO nanofluid. RL22H was the base oil used to disperse Al$_2$O$_3$ and ZnO nanoparticles while RL68H was used to disperse CuO and ATO nanoparticles. An additional nanofluid with 20nm Al$_2$O$_3$ nanoparticles dispersed in RL68H at the mass fraction of 0.50% was also tested for heat transfer performance during flow boiling. Different combinations of parameters that were used to create nanofluids in the study are given in Table 3.4. As mentioned earlier, all oil-based nanoparticle dispersions were procured from Nanophase Inc. and then mixed with R134a to create respective nanofluids.

3.6.1 Al$_2$O$_3$/RL22H/R134a nanofluid

3.6.1.1 Effect of particle mass fraction

Alumina nanofluids were prepared using Al$_2$O$_3$/RL22H dispersion, 40% in mass fraction. Highest particle mass fraction of 1.34% was obtained in nanofluid using the available dispersion. The dispersion was diluted with RL22H to 20%, 10%, and 4% to obtain nanofluids with particle mass fractions of 0.5, 0.22 and 0.08%, respectively. The mass fraction of RL22H was kept constant at 2% in all the experiments. The mass of R134a used to create each nanofluid for respective dispersion was 3.02kg.

Results from flow boiling heat transfer experiments of Al$_2$O$_3$/RL22H/R134a nanofluid at different particle mass fractions are shown in Figure 3.6. Comparisons of $h$ were made with respective baseline data. No significant improvement was observed with the use of nanoparticles in oil/refrigerant mixture. The average increase in $h$ at the mass fraction of 0.08% was 1.7%. For higher mass fractions, decrease in heat transfer performance was observed. The average decreases in $h$ at the particle mass fractions of 0.22, 0.5, and 1.34% were 4.5, 8.5, and 15%, respectively. So, the heat transfer performance deteriorated with increases in particle mass.
fraction. For the nanofluids showing decreases in $h$, small increases in $k$ and significant increases in $\mu$ were observed. The increase in viscosity indicated increase in surface tension and led to decreases in $h$ during flow boiling of oil/R134a mixture during baseline experiments. It is highly probable that the increase in viscosity in addition to the presence of nanoparticles were responsible for decreases in $h$ for nanofluids. Increase in viscosity as high as 529% was observed in Al$_2$O$_3$ nanofluids. The corresponding predicted increase in surface tension using empirical correlation for pure R134a was 170%. Decreases in $h$ can be explained by increases in viscosity at the particle mass fractions of 0.22 and 0.5%. However, at the particle mass fraction of 1.34%, additional decrease in $h$ was observed even without an additional increase in viscosity. This indicates that the nanoparticles were also responsible for observed decreases in $h$. The decreases in heat transfer did not exhibit strong correlation with heat flux or mass flux. The average absolute deviation (AAD) of $h$ from their baseline increased with increases in particle mass fraction indicating larger scatter in $h$ and stochastic nature of the nanoparticle interaction during flow boiling.

The flow boiling apparatus was cleaned using acetone after every nanofluid experiment and the baseline experiments were repeated. No significant change in the baseline heat transfer was observed indicating that the test section surface was not permanently modified due to use of nanofluids and deposition of nanoparticles. Validating baseline data after every mass fraction of nanofluid also ensured that the change in heat transfer performance was only because of the corresponding nanofluid. The pressure drop in the test section did not show measurable deviation from its baseline at the corresponding mass fluxes due to use of nanofluids.

3.6.1.2 Effect of quality

The decreases in $h$ for nanofluids correlated strongly with quality as compared to the heat flux or mass flux. To investigate the effect of quality on heat transfer performance of nanofluid, percentage change in $h$ were plotted against quality for the highest particle mass fraction of nanofluid and are shown in Figure 3.7a. It is evident from the plot that the decreases in $h$ are significant at low and moderate qualities while minimal at higher qualities. The flow boiling heat transfer is generally expressed as a combination of nucleate boiling and convective boiling contributions [48, 76]. To understand the physical mechanism responsible for decreases in $h$, it is
important to find the dominant mechanism of heat transfer at the experimental conditions. Minimum heat flux for the onset of nucleate boiling [49] can be predicted using

\[ q_{ONB} = \frac{2\sigma T_{sat} h_{Lr}}{r_{cr} \rho_g i_{fg}} \]  

(3.14)

where \( \sigma \) is the surface tension, \( T_{sat} \) is the saturation temperature in K, \( h_{Lr} \) is the convective heat transfer coefficient based on total flow as liquid, \( r_{cr} \) is the critical bubble radius (0.3\( \mu \)m is the recommended value for drawn tubes), \( \rho_g \) is the density of vapor and \( i_{fg} \) is the enthalpy of evaporation. It was found that 92% of the experimental data met the requirement for the onset of nucleate boiling using the properties of pure R134a.

Nucleate boiling is the dominant mechanism of heat transfer at experimental conditions that exhibit significant decreases in \( h \). The ratios of nucleate boiling to convective boiling contributions for the experimental conditions in Figure 3.7a are plotted in Figure 3.7b using a predictive model by Kattan et al. [17]. The predictions plotted in Figure 3.7b are for pure R134a and indicate nucleate boiling to be the dominant mechanism at low and moderate qualities. The nucleate boiling contribution is expected to increase further at these qualities due to the presence of oil as observed from experimental data in Figure 3.4b and Figure 3.5a. So it can be hypothesized that the decrease in flow boiling heat transfer of nanofluids was observed due to suppression or delay of nucleation mechanism. The primary mechanism that might delay or suppress nucleation is increase in viscosity of nanofluid corresponding to the respective base fluid which was explained in previous section. However, this mechanism should be coupled with a secondary mechanism that can explain decrease in \( h \) without increase in viscosity at the highest particle mass fraction of Al\(_2\)O\(_3\) nanofluid. This secondary mechanism must be of nanoparticles filling up the micro-cavities that results in a loss of nucleation sites as reported in literature [34, 37, 51]. In this study, however, the Al\(_2\)O\(_3\) nanoparticles did not permanently modify the test surface and the baseline heat transfer performance was regained after cleaning with acetone. It is possible that in a stable nanofluid with no agglomeration and settlement of nanoparticles, the loss of nucleation sites is not due to the permanent filling of micro-cavities but to the net flux of nanoparticles in micro-cavities. This would suggest that the nucleation sites are activated and suppressed intermittently due to dynamic change in surface roughness during flow boiling of
nanofluid. Higher mass fraction of nanofluid thus showed pronounced decrease in $h$ as more nanoparticles were available to effectively fill micro-cavities. Secondary nucleation on nanoparticles is also expected to play a role during boiling of nanofluids [44]. However, it may not be important due to delayed nucleation and increased $q_{ONB}$ resulting from increased viscosity and surface tension.

3.6.1.3 Effect of particle size and particle number density

The effect of particle size on heat transfer performance during flow boiling of nanofluids was observed using particle sizes of 20nm and 40nm. Same surface treatment and base oil were used to create the two nanofluids. Particle mass fraction in 20nm Al$_2$O$_3$/RL22H/R134a nanofluid was 1.34% while that in 40nm Al$_2$O$_3$/RL22H/R134a nanofluid was 1.35%. The heat transfer performance of the two nanofluids is shown in Figure 3.8. Average decreases of 15 and 5% were observed in $h$ during flow boiling of 20 and 40nm nanofluids, respectively. It may appear that the heat transfer performance deteriorates with decrease in particle size. The increases in $k$ were 2.3 and 2% while increases in $\mu$ were 436 and 298% for 20nm and 40nm nanofluids, respectively. The significantly higher increase in $\mu$ for 20nm nanofluid suggests more severe suppression or delay in nucleation due to primary mechanism.

The effect of secondary mechanism on heat transfer should vary with the number of particles in the nanofluid and not with the particle mass fraction when comparing nanofluids of different particle sizes. Particle number density was calculated based upon the number of nanoparticles in each nanofluid and the total volume of the flow boiling apparatus. Particle number density of 20nm nanofluid was eight times higher than that of 40nm nanofluid, assuming that the true density of Al$_2$O$_3$ nanoparticles was same in both cases. The particle number density is expected to alter the efficiency of filling up of micro-cavities on the test section surface, thus suppressing nucleation due to the secondary mechanism. So combining the two effects, average decreases in $h$ of 15 and 5% were observed with increases in viscosity of 436 and 298%, and particle number densities of 611 and 77/µm$^3$. The average decreases in $h$ were comparable for the nanofluids with similar particle number densities but different particle sizes. An average decrease in $h$ was 4.5% for the particle number density of 99/µm$^3$ in case of 20nm nanofluid and the decrease was 5% for the particle number density of 77/µm$^3$ in case of 40nm nanofluid. The increase in viscosity for the two nanofluids was approximately same. In earlier results decreases
in $h$ by 4.5, 8.5, and 15% were observed for particle mass fractions of 0.22, 0.50, and 1.34% which correspond to the particle number densities of 99, 228, and 611/$\mu$m$^3$ and increases in viscosity of 310, 529, and 436%, respectively. These results indicate that the primary mechanism induced due to increased viscosity is necessary in delaying the nucleation process; however, the magnitude of decrease in $h$ is a stronger function of particle number density and not the increase in viscosity.

3.6.2 ZnO/RL22H/R134a nanofluid

Effects of different nanoparticles on flow boiling of R134a-based nanofluids were observed. Experiments with variation in multiple parameters with Al$_2$O$_3$ nanofluid exhibited significant decrease in $h$ during flow boiling. Deterioration in $h$ was more pronounced at the highest particle mass fraction used in Al$_2$O$_3$ nanofluid. So, experiments with ZnO nanofluids were conducted only at that particle mass fraction to compare the effects of two different nanoparticles. The surface treatment and the base oil used in the preparation of nanofluids were unchanged. Results from heat transfer performance of 20nm ZnO/RL22H/R134a nanofluid, 1.34% in particle mass fraction, are shown in Figure 3.9a. An average decrease of 22% was observed in $h$ during flow boiling. The decrease was higher than that observed with 20nm Al$_2$O$_3$ nanofluid at similar mass fraction and showed similar variation with quality. The increase in viscosity for ZnO nanofluid was 312% compared to 436% for Al$_2$O$_3$ nanofluid. The primary mechanism of delay in nucleation process was at play in both nanofluids. However, ZnO nanoparticles were observed to coat the surface of the flow boiling apparatus. The observation was made using a sight glass placed after the copper test section. Al$_2$O$_3$ nanofluids did not show such coating on sight glass. It is possible that the particle-surface adhesion was stronger in case of ZnO nanoparticles leading to deposition on the surfaces of flow boiling apparatus. However, the surfaces of flow boiling apparatus were easily cleaned with circulation of acetone and matched their baseline performance after cleaning.

A 40nm ZnO/RL22H/R134a nanofluid, 1.34% in mass fraction, was also used for flow boiling. Results of $h$ during flow boiling are shown in Figure 3.9b. The average decrease in $h$ in this case was 8.5% and compares well with decrease of 5% for 40nm Al$_2$O$_3$ nanofluid with the same mass fraction. The hypothesis that the secondary mechanism for suppression of nucleate boiling which depends largely on particle number density plays a significant role in the flow
boiling of nanofluids holds very well with these results. In ZnO nanofluids, decreases in \( h \) of 22 and 8.5\% were observed at particle number densities of 447 and 56/\( \mu \)m\(^3\). The decreases in viscosity for the corresponding nanofluids were 312 and 381\%, respectively. This confirms that even though the primary mechanism delays the nucleation process, the magnitude of decrease in \( h \) due to suppression of nucleation is a strong function of particle number density and not the increase in viscosity. The decreases in \( h \) were comparable to those observed in \( \text{Al}_2\text{O}_3 \) nanofluids at similar particle number densities. The additional decrease in \( h \) observed in \( \text{ZnO} \) nanofluids can be attributed to the particle-surface adhesion that allows nanoparticles to coat the heat transfer surface.

3.6.3 CuO/RL68H/R134a nanofluid

CuO nanoparticles, 20nm in size, were used to create nanofluids due to their slightly better thermal conductivity. RL68H was used as the base oil because CuO/RL68H/R134a nanofluid had shown marked improvement in flow boiling heat transfer performance in literature [35]. A different surface treatment (also Nanophase proprietary) than that used with \( \text{Al}_2\text{O}_3 \) and \( \text{ZnO} \) nanoparticles was required to get stable dispersion in oil. Even though the new surface treatment yielded stable dispersion in oil, only partially stable nanofluid was obtained with R134a. Agglomeration and particle settlement were observed in the nanofluid over time. Nonetheless, experiments with two different particle mass fractions of CuO nanofluids were conducted. It was possible that due to partial stability of the nanofluid, a nanoparticle-rich layer near the heat transfer surface might result in better heat transfer performance during flow boiling as found in the literature for pool boiling experiments [44].

Heat transfer experiments without thermal property measurements were conducted with CuO nanofluid, 0.08\% in particle mass fraction. At the same particle mass fraction, \( \text{Al}_2\text{O}_3 \) nanofluid exhibited a small increase in \( h \). An average decrease of 7\% was observed in \( h \) during flow boiling of CuO nanofluid and the comparison is shown in Figure 3.10a. The decreases in \( h \) were quite significant considering the low particle mass fraction and might have been caused due to poor stability of dispersion. Dark black CuO nanoparticles coated the surface of the flow boiling apparatus. The same cleaning process as used during \( \text{Al}_2\text{O}_3 \) and \( \text{ZnO} \) nanofluids was used to clean the flow boiling apparatus and the baseline experiments were repeated. The results from the comparison are shown in Figure 3.10b and exhibit significant decreases in \( h \) after the
cleaning process, indicating that the test section was modified due to the use of CuO nanofluid. Average decrease in the baseline $h$ before and after the use of CuO nanofluid was 5.5%. CuO nanoparticles, unlike Al$_2$O$_3$ and ZnO nanoparticles, were not cleaned away by acetone and filled the micro-cavities of the test section causing the secondary mechanism to deteriorate the baseline heat transfer performance.

The same test section was used without further cleaning to evaluate heat transfer performance of CuO nanofluid, 0.22% in particle mass fraction. Thermal properties of CuO nanofluid were measured in this case and showed significant increase in both thermal conductivity and viscosity. Increase in $k$ was 12.6% while that in $\mu$ was 2147% over the baseline. These increases were an order of magnitude higher than those observed in other nanofluids including the ones with higher particle mass fraction. Experimental results for flow boiling of 0.22% CuO nanofluid are shown in Figure 3.11a and indicate an average decrease of only 2.7%. The decreases in $h$ were not observed at heat fluxes of 5, 10 and 15kW/m$^2$, and averaged to 6% and 13.7% at the heat flux of 20 and 25kW/m$^2$, respectively. This can be explained using primary mechanism: nucleation was active at higher heat fluxes for flow boiling of oil/R134a mixture over CuO-fouled surface but was inactive for all the heat fluxes in case of 0.22% CuO nanofluid due to significant increase in viscosity and surface tension (not measured). Higher decrease in $h$ was not apparent for higher particle mass fraction for CuO nanofluid because the baselines were not consistent in the two cases. As it was observed that the cleaning process used in previous nanofluids was not effective in cleaning CuO nanofluid, the process was repeated three times after the experiments with 0.22% CuO nanofluid. Comparison of baseline $h$ before and after the use of nanofluids in this case is shown in Figure 3.11b. The results show that the repetitive cleaning process was useful and the baseline $h$ in fact showed an average improvement of 5% over previous baseline $h$. The results from baseline 3, even though similar to baseline 1 in average, did not exactly match baseline 1 and showed improvement at some experimental conditions while deterioration at others. The average difference between the baseline 3 and baseline 1 was only 0.1% but the average absolute deviation was 8.8%. This indicated that the test section was modified due to CuO nanoparticles even though the average heat transfer performance did not change significantly.

3.6.4 Al$_2$O$_3$/RL68H/R134a nanofluid
Both RL22H and RL68H-based dispersions exhibited decrease in $h$ during flow boiling with different nanoparticles. To understand and compare the effect of the two POE oils on heat transfer performance of nanofluids, $\text{Al}_2\text{O}_3$/RL68H/R134a nanofluid was created using exactly the same surface treatment. The effect of POE oils in oil/R134a mixtures was studied during baseline experiments. A particle mass fraction of 0.5% that was used in $\text{Al}_2\text{O}_3$/RL22H/R134a nanofluid was selected. Thermal properties of the nanofluid were measured; $k$ and $\mu$ showed increases of 0.7 and 203%, respectively. In comparison, the increase was 1.4% in $k$ and 529% in $\mu$ for $\text{Al}_2\text{O}_3$/RL22H/R134a nanofluid with similar mass fraction. The increases in both $k$ and $\mu$ for RL68H-based nanofluid were approximately half of those in RL22H-based nanofluid.

Experimental $h$ from flow boiling of $\text{Al}_2\text{O}_3$/RL68H/R134a nanofluid were compared with their baseline and are shown in Figure 3.12. An average decrease of only 0.6% was observed. The average decrease was 8.5% for $\text{Al}_2\text{O}_3$/RL22H/R134a nanofluid. It is evident that the primary mechanism due to increase in viscosity and predicted increase in surface tension was significantly higher in RL22H-based nanofluid. However, it does not fit the earlier hypothesis that the primary mechanism is only a requirement and the magnitude of decrease in $h$ is a strong function of particle number density. A part of the reason can be the residual surface modification of copper test section due to CuO nanoparticles in previous experiment. If the CuO nanoparticles already filled the micro-cavities in the test section during the baseline experiment for $\text{Al}_2\text{O}_3$/RL68H/R134a nanofluid, $\text{Al}_2\text{O}_3$ nanoparticles cannot deteriorate the heat transfer performance further during nanofluid experiment.

3.6.5 $\text{ATO}$/RL68H/R134a nanofluid

ATO nanoparticles, 20nm in size, were used due to their availability and dispersion stability in R134a. They also provided new particle material for the current study. Similar surface treatment used in $\text{Al}_2\text{O}_3$ and ZnO nanoparticles was used on ATO nanoparticles. The particle mass fraction in $\text{ATO}$/RL68H/R134a nanofluid was 0.22%. Thermal properties of ATO nanofluid were measured; $k$ increased minimally by 0.3% and $\mu$ decreased by 22%. This was the only nanofluid that exhibited decrease in viscosity due to addition of nanoparticles. Experimental $h$ during flow boiling of ATO nanofluid was compared with the baseline and is shown in Figure 3.13a. Measureable increases in $h$, as high as 35% and an average of 10%, were observed. The increases can be explained with the primary mechanism: reduced viscosity and surface tension
leading to enhanced nucleation process during flow boiling. The secondary mechanism of suppression of nucleation due to nanoparticles filling up micro-cavities was not as effective due to fouling of test section with CuO nanoparticles. This was evident during previous experiments with Al₂O₃/RL68H/R134a nanofluid.

In order to further verify and distinguish between convective and nucleate boiling mechanisms, heat transfer experiments were conducted during single-phase flow of ATO nanofluid. Experiments were carried out by increasing the subcooling by 20 to 35°C and making sure that the nanofluid temperature was at least 5°C lower than the saturation temperature at all experimental conditions. Results were then compared with baseline for similar heat flux and mass flux conditions. The comparison of $h$ during convective heat transfer of ATO nanofluid is shown in Figure 3.13b. A consistent increase was observed in $h$ at different experimental conditions and averaged to 8%. The Dittus-Boelter correlation can be used to predict $h$ during convective heat transfer in fully developed turbulent flows. For a decrease of 22% in $\mu$ and constant mass flux, the correlation predicts an increase of 7.7% in convective heat transfer which compares well with the measured average value of 8%. The increase in the convective boiling contribution during flow boiling can be safely assumed to be of the similar magnitude. At most of the experimental conditions in this study, heat transfer on wetted perimeter is significantly higher than that on dry surface. Heat transfer on wetted perimeter is in turn comprised of convective and nucleate boiling contributions. With an assumption that the nucleate and convective boiling contributions are similar in magnitude during most of the experimental conditions, 8% increase in convective boiling leads to approximately 4% increase in heat transfer on wetted perimeter. With a more realistic assumption that the convective boiling contribution is only half of nucleate boiling, 8% increase in it leads to only 1% increase in heat transfer on wetter perimeter. This indicates that the enhancement in nucleate boiling contributes significantly to the enhancement in flow boiling heat transfer of ATO nanofluid.

It was observed from a number of nanofluids used in this study that the increase in viscosity and predicted increase in surface tension delayed nucleation and onset of nucleate boiling leading to deterioration in heat transfer performance during nucleate boiling dominated flows. Similarly, decrease in viscosity can lead to enhanced nucleation at available sites. The suppression of nucleate boiling due to filling up of micro-cavities did not seem to cause adverse effects in this case mostly because CuO-fouled surfaces were used to obtain baseline $h$. It is
possible that with the use of clean test section, the enhancements in $h$ due to primary mechanism promoting nucleation will be negated by suppression of nucleation due to secondary mechanism. An additional mechanism that might also work in favor of enhancements is of secondary nucleation on the nanoparticle surface due to primary mechanism facilitating nucleation.

3.7 Conclusions

- Stable R134a-based nanofluids were created using proprietary surface treatments. POE oils were used to create stable dispersions which were then mixed with R134a to create nanofluids.
- The thermal properties of R134a-based nanofluids were measured and showed significant changes in viscosity from the baseline oil/R134a mixtures. Highest increase of 2147% was observed due to CuO nanoparticles while ATO nanoparticles were the only particles to exhibit decrease in measured viscosity of 22%. Increases in viscosity due to Al$_2$O$_3$ and ZnO nanoparticles ranged from 200 to 530%. The viscosity did not increase linearly with particle mass fraction in case of Al$_2$O$_3$ nanofluid.
- A small increase in thermal conductivity was observed in all R134a-based nanofluids. The highest increase in conductivity was 13% for CuO nanoparticles. The thermal conductivity was observed to increase almost linearly with particle mass fraction in case of Al$_2$O$_3$ nanofluid.
- Heat transfer during flow boiling of R134a-based nanofluids showed deterioration for all the nanoparticles that caused increase in the viscosity. ATO nanoparticles caused decrease in viscosity leading to favorable nucleation and thus enhancement during flow boiling. Change in viscosity and predicted change in surface tension that modified nucleation process was the primary mechanism responsible for change in thermal performance during flow boiling. The primary mechanism also included change in the convective boiling heat transfer due to change in viscosity which constituted a smaller fraction of change to the two-phase flow heat transfer.
- An increase in particle number density correlated well with decrease in heat transfer during flow boiling for different particles as well as particle sizes. The secondary mechanism of suppression of nucleation boiling due to filling up of micro-cavities on test surface was quite significant for the clean surfaces. The magnitude of decrease in heat
transfer during flow boiling was better correlated with secondary mechanism when the primary mechanism was present. The secondary mechanism was not as effective in suppressing nucleate boiling on CuO-fouled surfaces due to possible unavailability of micro-cavities.

- An average decrease in heat transfer during flow boiling was 15% and 22% for Al₂O₃ and ZnO nanofluids, respectively. The highest decrease was observed at the highest particle mass fraction of 1.34% used in the study. CuO nanoparticles exhibited an averaged decrease of 7% for particle mass fraction of only 0.08%. An average increase of 10% was observed with ATO nanoparticles, 0.22% in particle mass fraction.

- Changes in the viscosity and possibly the surface tension play more important role in heat transfer performance of nanofluids than changes in thermal conductivity. Nanofluids should be screened using their thermal properties to obtain enhancements in heat transfer during two phase flows.
3.8 Figures and Tables

Figure 3.1: Schematic of the flow boiling apparatus

Figure 3.2: a) TEM image of 40nm Al₂O₃ nanoparticles (courtesy of Nanophase Inc.) b) Image of Al₂O₃/RL22H/R134a nanofluid through sight window of pressure vessel.
Figure 3.3: Comparison of flow boiling heat transfer coefficients of R134a with models available in literature.
Figure 3.4: a) Comparison of $h$ during flow boiling of RL22H/R134a mixture to pure R134a. b) Variation of $h$ ratio with and without RL22H against quality.
Figure 3.5: a) Variation of $h$ ratio with and without RL68H against quality. b) Comparison of $h$ during flow boiling of different POE oil mixtures in R134a.
Figure 3.6: Heat transfer performance during flow boiling of Al₂O₃/RL22H/R134a nanofluid at varying particle mass fraction.
Figure 3.6 (cont.)

(c) Nanofluid: Al₂O₃/RL22H/R134a
Particle size: 20 nm
Particle mass fraction: 0.50%

(d) Nanofluid: Al₂O₃/RL22H/R134a
Particle size: 20 nm
Particle mass fraction: 1.34%
Figure 3.7: a) Variation in % change in $h$ with change in quality. b) Model predictions of nucleate to convective boiling contributions for pure R134a.
Figure 3.8: Heat transfer performance during flow boiling of Al₂O₃/RL22H/R134a nanofluid at different particle sizes and particle number densities.
Figure 3.9: Heat transfer performance during flow boiling of ZnO/RL22H/R134a nanofluid at different particle sizes and particle number densities.
Figure 3.10: a) Heat transfer performance of 0.08% CuO nanofluid. b) Comparison of baselines before and after 0.08% CuO nanofluid experiment.
Figure 3.11: a) Heat transfer performance of 0.22\% CuO nanofluid. b) Comparison of baselines before and after 0.22\% CuO nanofluid experiment.
Figure 3.12: Heat transfer performance during flow boiling of Al₂O₃/RL68H/R134a nanofluid.
Figure 3.13: Heat transfer performance of ATO/RL68H/R134a nanofluid during a) flow boiling, b) convective heat transfer.
Table 3.1: Experimental conditions for flow boiling of nanofluids

<table>
<thead>
<tr>
<th>Variable</th>
<th>Range</th>
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<tr>
<td>Heat flux</td>
<td>5 to 25kW/m²</td>
</tr>
<tr>
<td>Mass flux</td>
<td>100 to 1000kg/m²s</td>
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<tr>
<td>Quality</td>
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<td>Saturation temperature</td>
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Table 3.2: Experimental uncertainty in recorded variables during flow boiling of nanofluids

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<th>Uncertainty</th>
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<td>Temperature</td>
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<tr>
<td>Pressure</td>
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<tr>
<td>Mass flow rate</td>
<td>± 0.1%</td>
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<td>Energy balance</td>
<td>± 5%</td>
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<tr>
<td>Heat transfer coefficients</td>
<td>± 10%</td>
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</table>
Table 3.3: Thermal properties of nanofluids

<table>
<thead>
<tr>
<th>Fluid</th>
<th>$T$ [°C]</th>
<th>$k$ [mW/m-K]</th>
<th>$\mu$ (mPa-s)</th>
</tr>
</thead>
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<tr>
<td>Water</td>
<td>12.4</td>
<td>572.2</td>
<td>0.93$^a$</td>
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<tr>
<td>R134a</td>
<td>20.7</td>
<td>94.6</td>
<td>0.28</td>
</tr>
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<td>RL22H</td>
<td>24.7</td>
<td>156.1</td>
<td>52.57</td>
</tr>
<tr>
<td>RL68H</td>
<td>24.9</td>
<td>143.1</td>
<td>244.59</td>
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<td>20nm Al$_2$O$_3$/RL22H (40.14% wt)</td>
<td>24.8</td>
<td>257.7</td>
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<tr>
<td>RL22H/R134a (2.12% wt)</td>
<td>24.5</td>
<td>92.6</td>
<td>1.23</td>
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<td>20nm Al$_2$O$_3$/RL22H/R134a (0.23% wt)</td>
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<td>93.6</td>
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<td>20nm Al$_2$O$_3$/RL22H/R134a (0.55% wt)</td>
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<td>20nm Al$_2$O$_3$/RL22H/R134a (1.41% wt)</td>
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<td>40nm Al$_2$O$_3$/RL22H/R134a (1.43% wt)</td>
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<tr>
<td>20nm CuO/RL68H/R134a (0.24% wt)</td>
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<td>20nm Al$_2$O$_3$/RL68H/R134a (0.53% wt)</td>
<td>23.3</td>
<td>93.6</td>
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<td>20nm ATO/RL68H/R134a (0.25% wt)</td>
<td>24.1</td>
<td>93.2</td>
<td>1.10</td>
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</table>

$^a$ Measured at 21.6°C
Table 3.4: Combination of parameters to create nanofluids for the study

<table>
<thead>
<tr>
<th>Particle</th>
<th>Oil</th>
<th>Refrigerant</th>
<th>Particle size (nm)</th>
<th>Surface treatment</th>
<th>Particle mass fraction (%)</th>
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<td>Al$_2$O$_3$</td>
<td>RL22H</td>
<td>R134a</td>
<td>20</td>
<td>Polar</td>
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<td>R134a</td>
<td>40</td>
<td>Polar</td>
<td>1.35</td>
</tr>
<tr>
<td>ZnO</td>
<td>RL22H</td>
<td>R134a</td>
<td>20</td>
<td>Polar</td>
<td>1.34</td>
</tr>
<tr>
<td>ZnO</td>
<td>RL22H</td>
<td>R134a</td>
<td>40</td>
<td>Polar</td>
<td>1.34</td>
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<tr>
<td>CuO</td>
<td>RL68H</td>
<td>R134a</td>
<td>20</td>
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<td>20</td>
<td>Polar</td>
<td>0.50</td>
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<tr>
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<td>RL68H</td>
<td>R134a</td>
<td>20</td>
<td>Polar</td>
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</tr>
</tbody>
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4.1 Introduction

Pressure drop plays an important role in designing heat transfer systems. Pumping power is directly proportional to the pressure drop in these systems. During flow boiling of refrigerants, pressure drop can be calculated as a combination of frictional, acceleration and gravitational components. Knowledge of void fraction, volume fraction of vapor in the flow, is important to evaluate pressure drop in two-phase flow. A number of models are available in the literature to evaluate void fraction and pressure drop during flow boiling of refrigerants [4]. In a refrigeration system, higher pressure drop in the evaporator means higher specific volume of the vapor at the inlet of the compressor leading to a drop in the mass flow rate. In low temperature suction lines, significant pressure drop can cause a drop in saturation temperature and thereby decrease the overall efficiency of the system.

Condenser subcooling is usually defined as the total temperature drop of refrigerant from its saturation temperature, which takes place in a condenser after the condensation process is complete. Subcooling is usually used in refrigeration cycle for the proper functioning of the expansion valve by making sure that the refrigerant is in liquid state before entering the device. Subcooling in refrigeration systems is quite important and in some cases heat exchangers with the sole purpose of achieving it are installed. In a few cases, it is coupled with the superheating process before the compressor using an internal heat exchanger. As the condenser subcooling increases, COP of the system is shown to undergo a maximum which is a result of trade-off between increasing refrigerating effect and increasing specific compression work [77].

4.2 Pressure drop

Pressure drop during flow boiling of nanofluids in the copper test section, 6.23mm in diameter and 1.8m in length, was measured and cast in terms of pressure drop per unit length, $\Delta P/L$. The experimental uncertainty in these measurements was ±1.2kPa/m. The measured pressure drop for each nanofluid was compared with the respective pressure drop from the base fluid. The comparisons were made at similar controllable experimental conditions of mass flux, heat flux, fluid temperature and pressure. The fluid inlet conditions were very close to each other for each base fluid and the corresponding nanofluid. However, due to change in $h$ during flow...
boiling of nanofluid, the exit quality of the nanofluid was slightly different than that in case of the base fluid. The measured pressure drop in both cases was combination of single-phase flow during initial subcooled conditions and two-phase flow during flow boiling in the test section. The two-phase pressure drop can be further divided into frictional, acceleration, and gravitational components. The total pressure drop in the test section was not divided into these components as the uncertainty in measurements was high. The difference in the exit quality of the base fluid and nanofluid was also ignored and no corrections were made to the recorded measurements to account for it.

The experimental data for pressure drop of CO$_2$-based nanofluids are shown in Error! Reference source not found. and compares $\Delta P/L$ of CuO/CO$_2$ and TiO$_2$/CO$_2$ nanofluids with their respective baselines. The measurement uncertainty was high; 50% or more in almost all the measurements due to small pressure drop in CO$_2$-based nanofluids. The effect of high measurement uncertainty can be observed in both CO$_2$-based nanofluids at low $\Delta P/L$ measurements in which the deviations from the baseline were significant; increases and decreases of over 100% of the baseline measurements were observed. So, a detailed analysis of CO$_2$-based nanofluids may not lead to concrete conclusions for pressure drop changes due to addition of nanoparticles to the base fluid.

For R134a-based nanofluids, even with significant increase in viscosity, $\Delta P/L$ did not show significant deviation from baseline. For Al$_2$O$_3$/RL22H/R134a nanofluids, $\Delta P/L$ at different particle mass fractions is shown in Figure 4.2. $\Delta P/L$ increased due to the use of nanoparticles at the lowest particle mass fraction, however, a consistent decrease was observed at higher particle mass fractions. The average increase in $\Delta P/L$ was 4.9% for the particle mass fraction of 0.08%. Average decreases in $\Delta P/L$ for the particle mass fractions of 0.22, 0.5, and 1.34% were 3.5, 5.4, and 6.2%, respectively. Decrease in the observed $\Delta P/L$ might seem uncharacteristic for these nanofluids as they exhibit increase in viscosity. However, $\Delta P/L$ was not compared at similar $Re$ in which case nanofluid with high viscosity would require higher mass flow rate to attain similar values of $Re$ and thus exhibit higher values of $\Delta P/L$. The values of $\Delta P/L$ were compared with the baseline at constant mass flow rate or constant mass flux or constant product of density and velocity. The density of nanofluids and the base fluid was measured in this study at subcooled conditions using a Coriolis-effect flow meter with an uncertainty of ±1kg/m$^3$. The density of the nanofluids increased consistently with increases in particle mass fraction as expected. The
average increases in the density for nanofluids with particle mass fractions of 0.08, 0.22, 0.5, and 1.34% were 0.05, 0.16, 0.39, and 1.02%, respectively. A small increase in the density indicates a small decrease in the velocity of the nanofluid compared to the base fluid for a constant mass flux condition. This decrease in fluid velocity can lead to decrease in frictional pressure drop, thus decreasing $\Delta P/L$ for nanofluids.

$\Delta P/L$ comparison for $\text{Al}_2\text{O}_3/\text{RL}22\text{H}/\text{R}134\text{a}$ nanofluids with different particle sizes is shown in Figure 4.3. Average decreases of 6.2 and 5.1% in $\Delta P/L$ and average increases of 1.02 and 0.86% in density were observed for the particles sizes of 20 and 40nm, respectively. For $\text{ZnO}/\text{RL}22\text{H}/\text{R}134\text{a}$ nanofluids, comparison of $\Delta P/L$ at different particle sizes is shown in Figure 4.4. The average increases in density were 0.5 and 0.77% for the particle sizes of 20 and 40nm, respectively. However, an increase in $\Delta P/L$ was observed for $\text{ZnO}/\text{RL}22\text{H}/\text{R}134\text{a}$ nanofluids. The average increases were 10.8 and 4.9% for the particle sizes of 20 and 40nm, respectively. Comparison of $\Delta P/L$ with the baseline for different particle mass fractions of $\text{CuO}/\text{RL}68\text{H}/\text{R}134\text{a}$ nanofluid is shown in Figure 4.5. A small average decrease of 0.2% while an average increase of 11.5% were observed in $\text{CuO}/\text{RL}68\text{H}/\text{R}134\text{a}$ nanofluid at the particle mass fractions of 0.08 and 0.22%, respectively. The average increases in density for the corresponding mass fractions of nanofluids were 2.96 and 1.32%. $\text{CuO}/\text{RL}68\text{H}/\text{R}134\text{a}$ nanofluids were not stable and showed significant deposition of nanoparticles on the surface of the flow boiling apparatus. Baseline data for $h$ after the use of 0.08% mass fraction of CuO nanofluid did not match the one before the use of nanofluid. Similar behavior was observed for the baseline data for density; an average increase in density of 1.33% was observed between the baseline measurements before and after the use of 0.08% CuO nanofluid. This can explain smaller increase in density for the 0.22% CuO nanofluid. Finally, $\Delta P/L$ comparisons for $\text{Al}_2\text{O}_3/\text{RL}68\text{H}/\text{R}134\text{a}$ and ATO/RL68H/R134a nanofluids are shown in Figure 4.6. For 20nm $\text{Al}_2\text{O}_3/\text{RL}68\text{H}/\text{R}134\text{a}$ nanofluid, 0.5% in particle mass fraction, average increase in density was 0.44% while the average decrease in $\Delta P/L$ was 5.1%. These values compare well with the values from 20nm $\text{Al}_2\text{O}_3/\text{RL}22\text{H}/\text{R}134\text{a}$ nanofluid of similar mass fraction. For ATO/RL68H/R134a nanofluid, 0.22% in particle mass fraction, average increase in density was 0.28% while average increase in $\Delta P/L$ was 3.2%. Based on the uncertainty and measured values of $\Delta P/L$ for various nanofluids, it can be concluded that the pressure drop during flow boiling of nanofluids did not
show significant deviation from its baseline. So, a decrease in $h$ was recorded for similar $\Delta P/L$ for a number of nanofluids used in this study.

4.3 Condenser subcooling

As mentioned before, condenser subcooling is defined as the total temperature drop of refrigerant from its saturation temperature, which takes place in a condenser after the condensation process is complete. A brazed plate heat exchanger was used as the condenser in this study. A detailed analysis on the condenser performance was not carried out; however, degree of subcooling achieved in the condenser was measured for all the nanofluids. The condenser was designed to provide the subcooled fluid during all experimental conditions. The temperature at the exit of the condenser was measured using a sheath-type thermocouple and the saturation temperature was evaluated using the absolute pressures at the inlet and exit of the condenser with an assumption that the nanoparticles do not affect the saturation state. For the same inlet conditions, degree of subcooling achieved in the condenser can be used as an indicator of its performance. Higher subcooling indicated better heat transfer while lower subcooling indicated poor heat transfer performance due to the use of nanofluids. However, the state of the nanofluid at the inlet of the condenser was not exactly similar to that of the base fluid due to different heat transfer performance in the evaporator test section. So the comparison of subcooling for various nanofluids in this study is not the best indicator of condensation heat transfer of these nanofluids. It can be, at best, used as an eyeball test for the performance of a brazed plate heat exchanger as a condenser for various nanofluids. Degree of subcooling for both CO$_2$ and R134a-based nanofluids was compared with their respective baselines and shown in Figure 4.7 to Figure 4.12. The experimental uncertainty in the measured subcooling was 0.2°C. It can be observed from the experimental results that the condenser performance was not affected significantly due to the use of nanofluids. The small deviations from the baseline that are observed can be attributed to the changes in the inlet flow conditions of the condenser.
4.4 Figures and Tables

Figure 4.1: Pressure drop during flow boiling of a) CuO/CO₂ and b) TiO₂/CO₂ nanofluids.
Figure 4.2: Pressure drop during flow boiling of Al$_2$O$_3$/RL22H/R134a at different particle mass fractions.
Figure 4.2 (cont.)

(c) Nanofluid: $\text{Al}_2\text{O}_3$/RL22H/R134a
Particle size: 20 nm
Particle mass fraction: 0.50%

(d) Nanofluid: $\text{Al}_2\text{O}_3$/RL22H/R134a
Particle size: 20 nm
Particle mass fraction: 1.34%
Figure 4.3: Pressure drop during flow boiling of Al$_2$O$_3$/RL22H/R134a nanofluid at different particle sizes and particle number densities.
Figure 4.4: Pressure drop during flow boiling of ZnO/RL22H/R134a nanofluid at different particle sizes and particle number densities.
Figure 4.5: Pressure drop during flow boiling of CuO/RL68H/R134a nanofluid at different particle mass fractions.
Figure 4.6: Pressure drop during flow boiling of a) $\text{Al}_2\text{O}_3$/RL68H/R134a and b) ATO/RL68H/R134a nanofluids.
Figure 4.7: Subcooling during condensation of a) CuO/CO\(_2\) and b) TiO\(_2\)/CO\(_2\) nanofluids in a brazed plate heat exchanger.
Figure 4.8: Subcooling during condensation of Al₂O₃/RL22H/R134a nanofluid at different particle mass fractions in a brazed plate heat exchanger.
Figure 4.8 (cont.)

(c) Nanofluid: Al₂O₃/RL22H/R134a  
Particle size: 20 nm  
Particle mass fraction: 0.50%

(d) Nanofluid: Al₂O₃/RL22H/R134a  
Particle size: 20 nm  
Particle mass fraction: 1.34%
Figure 4.9: Subcooling during condensation of Al₂O₃/RL22H/R134a nanofluid at different particle sizes in a brazed plate heat exchanger.
Figure 4.10: Subcooling during condensation of ZnO/RL22H/R134a nanofluid at different particle sizes in a brazed plate heat exchanger.
Figure 4.11: Subcooling during condensation of CuO/RL68H/R134a nanofluid at different particle mass fractions in a brazed plate heat exchanger.
Figure 4.12: Subcooling during condensation of a) Al₂O₃/RL68H/R134a and b) ATO/RL68H/R134a nanofluids in a brazed plate heat exchanger.
CHAPTER 5: CONCLUSIONS

An experimental investigation of flow boiling of refrigerant-based nanofluids was conducted. The two refrigerants used in the study were CO$_2$ and R134a. The refrigeration industry is currently considering options to reduce the amount of refrigerant in systems, make them compact and promote the use of environment-friendly refrigerants. Enhancing the thermal performance of CO$_2$ and R134a is in line with these objectives. Nanofluids primarily aim at enhancing thermal properties of the base fluids. They also introduce new physical mechanisms that affect thermal performance during two-phase flow.

Experimental apparatus to create and observe stability of refrigerant-based nanofluids was designed and fabricated. The creation of stable dispersions of nanoparticles in refrigerants presents challenges. Use of readily available nanoparticles to create refrigerant-based nanofluids by mixing and stirring was not successful. Only two partially stable nanofluids were obtained in CO$_2$ using CuO and TiO$_2$ nanoparticles. No stable dispersion was obtained in R134a using this approach. For R134a, nanoparticles were stabilized in POE oils using five different surface treatments and then assessed for stability in refrigerant. One proprietary surface treatment yielded stable dispersion in R134a and was used extensively in this study. Al$_2$O$_3$, ZnO, CuO, and ATO nanoparticles were used in different particle sizes and mass fractions to create R134a-based nanofluids.

Thermal properties of refrigerant-based nanofluids were measured. Thermal conductivity showed limited improvement due to use of nanoparticles. Most of the oxide nanoparticles that were used in the study had $k$ values in the range from 10 to 40W/m·K. The refrigerant thermal conductivity was on the order of 0.01W/m·K. The viscosity of refrigerant-based nanofluids exhibited significant increase. Even though increase in viscosity was expected, the magnitude of increase observed in this study was not expected.

Heat transfer performance of refrigerant-based nanofluids was observed using a closed loop flow boiling apparatus. The test section was a smooth copper tube, 6.23mm in diameter. Experimental $h$ values were measured in mass flux range from 100 to 1000kg/m$^2$·s, heat flux range from 5 to 25kW/m$^2$ and quality range from 0 to 1. Baseline experiments were carried out using pure CO$_2$ and oil/R134a mixture. Pressure drop in evaporator and degree of subcooling in the condenser were also measured during experiments.
5.1 CO\textsubscript{2}-based nanofluids

CuO and TiO\textsubscript{2} nanoparticles were used to create CO\textsubscript{2}-based nanofluids. CuO/CO\textsubscript{2} nanofluid did not show any significant change in $h$ during flow boiling. TiO\textsubscript{2}/CO\textsubscript{2} nanofluid showed significant decrease in $h$ during flow boiling compared to its baseline. An average decrease of 28\% was observed in $h$. The deterioration in $h$ was dependent on mass flux and showed marked improvement at mass fluxes above 400kg/m\textsuperscript{2}s. Pressure drop in the test section was unchanged with the use of nanofluids.

Nucleate boiling was the dominant mechanism of heat transfer during most experimental conditions. In TiO\textsubscript{2}/CO\textsubscript{2} nanofluid, it was conjectured that nanoparticles suppressed nucleate boiling at moderate qualities and showed deterioration in heat transfer performance. Modification to the existing flow regime map was proposed that limited decrease in $h$ to stratified-wavy flow and no significant change in $h$ during intermittent flow regime to accommodate sudden variation in $\%h$ at mass flux of 400kg/m\textsuperscript{2}s. Decrease in $h$ during flow boiling of TiO\textsubscript{2}/CO\textsubscript{2} nanofluid may be due to filling up of micro-cavities owing to the deposition of nanoparticles on the test surface. This can be corroborated with reduction in the mass fraction of nanoparticles after flow boiling experiments. The decrease in mass fraction of CuO nanoparticles was much smaller than that of TiO\textsubscript{2} nanoparticles in their respective nanofluids.

Nanofluids can significantly decrease heat transfer performance in evaporators. This result may not be general but specific to the size and surface treatment of TiO\textsubscript{2} nanoparticles used in this study. This is quite likely true for optimistic flow boiling results of nanofluids in literature. Generalized heat transfer performance results of nanofluids must be accepted and used with caution unless effect of multiple parameters such as particle, particle size, surface treatment, mass fraction and base fluid are systematically reported.

5.2 R134a-based nanofluids

This part of the study focused on overcoming shortcomings of the CO\textsubscript{2}-based nanofluids by using stable dispersions and assessing the effects of multiple parameters on heat transfer performance of nanofluids. Stable R134a-based nanofluids were created using proprietary surface treatments. POE oils were used to create stable dispersions which were then mixed with R134a to create nanofluids. Thermal properties of R134a-based nanofluids were measured and showed significant changes in viscosity from the baseline oil/R134a mixtures. Highest increase
of 2147% was observed due to CuO nanoparticles while ATO nanoparticles were the only particles to exhibit decrease in measured viscosity of 22%. Increases in viscosity due to Al₂O₃ and ZnO nanoparticles ranged from 200 to 530%. The viscosity did not increase linearly with particle mass fraction in case of Al₂O₃ nanofluid. Minimal increase in thermal conductivity was observed in all R134a-based nanofluids. The highest increase in conductivity was 13% for CuO nanoparticles. Thermal conductivity was observed to increase almost linearly with particle mass fraction in case of Al₂O₃ nanofluid.

Heat transfer during flow boiling of R134a-based nanofluids showed deterioration for all the nanoparticles that caused increase in the viscosity. ATO nanoparticles caused decrease in viscosity leading to favorable nucleation and thus enhancement during flow boiling. Change in viscosity and predicted change in surface tension that modified nucleation process was the primary mechanism responsible for change in thermal performance during flow boiling. Increase in particle number density correlated well with decrease in heat transfer during flow boiling for different particles as well as particle sizes. The secondary mechanism of suppression of nucleate boiling due to filling up of micro-cavities on test surface was quite significant for the clean surfaces. The magnitude of decrease in heat transfer during flow boiling was better correlated with secondary mechanism when the primary mechanism was present. The secondary mechanism was not as effective in suppressing nucleate boiling on CuO-fouled surfaces due to possible unavailability of micro-cavities.

An average decrease in heat transfer during flow boiling was 15% and 22% for Al₂O₃ and ZnO nanofluids, respectively. The highest decrease was observed at the highest particle mass fraction of 1.34% used in the study. CuO nanoparticles exhibited an average decrease of 7% for particle mass fraction of only 0.08%. An average increase of 10% was observed with ATO nanoparticles, 0.22% in particle mass fraction. Changes in the viscosity and possibly the surface tension play more important role in heat transfer performance of nanofluids than changes in thermal conductivity. Nanofluids should be screened using their thermal properties to obtain enhancements in heat transfer during two-phase flows.

5.3 Recommendations for future work

The thermal properties of refrigerant-based nanofluids play an important role in flow boiling. These properties can provide significant insight into predictions about heat transfer
behavior of these fluids. Apart from thermal conductivity and viscosity, surface tension of refrigerant-based nanofluids must be measured. These properties must be used as a screening process in case multiple refrigerant-based nanofluids are available for use.

Decrease or no significant increase in viscosity is indicative of better performance during nucleate boiling dominated two-phase flow in addition to improved convective heat transfer. Effect of viscosity on nucleate boiling of refrigerant-based nanofluids must be further studied to explore and validate physical mechanisms outlined in this study.

Nanoparticles with better thermal conductivity, like gold, silver and carbon nanotubes should be explored for flow boiling applications in refrigerants. Stable dispersion techniques and thermal properties of these nanofluids would be a good place to start the study.

Flow boiling of new refrigerant like R1234yf and R1234ze that are set to replace existing refrigerants must be evaluated for improvement using nanoparticles. As these refrigerants have properties very similar to that of R134a, creating stable dispersions using POE oils might be possible. However, viscosity of new refrigerant-based nanofluids must be carefully measured before further heat transfer analysis.

Condensation heat transfer of refrigerant-based nanofluids can be studied. The application of these fluids in microchannel heat exchangers used as evaporator as well as condenser should provide valuable and interesting results.

The research community needs to be more skeptical about the application of nanofluids in single-phase and two-phase flow applications. All the results must be carefully scrutinized before evaluating generalized claims of enhancements.
REFERENCES


[69] M. He, Y. Zhang, Q. Zhong, R. Xue, X. Zhang, Z. Liu, J. Fei, Thermophysical properties of 1,1,1,2-tetrafluorethane (CH₂FCF₃) refrigerant-oil mixtures in the saturated liquid phase with lubricant concentration in the range (0 to 100) ppm, Journal of Chemical and Engineering Data, 53(3) (2008) 710-715.


A sample code used for the data reduction in EES is provided below.

"Data Reduction code for flow boiling of R134-based nanofluids in a tube"

“Function to evaluate refrigerant quality”

function qualityref(i, i_f, i_g, P_TS_avg)
    if (i<=i_f) then
        x:=0;
    else
        if (i>=i_g) then
            x:=1;
        else
            x:=quality(r134a, h=i, P=P_TS_avg);
        endif
    endif
    qualityref:= x;
end

“Function to evaluate two phase flow length in sub-section A”

function calculatela(Q_sub, Q_TS)
    L_sub=Q_sub/Q_TS*1.738;
    if (L_sub>(0.167+0.25)) then
        L_a=0.0001;
    else
        if (L_sub>0.167) then
            L_a=0.25-(L_sub-0.167);
        else
            L_a=0.25;
        endif
    endif
end

106
function calculatelb(Q_sub, Q_TS)
    L_sub=Q_sub/Q_TS*1.738;
    if (L_sub>(0.167+0.5)) then
        L_b=0.0001;
    else
        if (L_sub>(0.167+0.25)) then
            L_b=0.25-(L_sub-(0.167+0.25));
        else
            L_b=0.25;
        endif
    endif
    calculatelb:=L_b;
end

function calculatelc(Q_sub, Q_TS)
    L_sub=Q_sub/Q_TS*1.738;
    if (L_sub>(0.167+0.75)) then
        L_c=0.0001;
    else
        if (L_sub>(0.167+0.5)) then
            L_c=0.25-(L_sub-(0.167+0.5));
        else
            L_c=0.25;
        endif
    endif
    calculatelc:=L_c;
end

“Function to evaluate two phase flow length in sub-section B”

“Function to evaluate two phase flow length in sub-section C”
“Function to evaluate two phase flow length in sub-section D”

function calculateld(Q_sub, Q_TS)
L_sub=Q_sub/Q_TS*1.738;
if (L_sub>(0.167+1)) then
L_d=0.0001;
else
if (L_sub>(0.167+0.75)) then
L_d=0.25-(L_sub-(0.167+0.75));
else
L_d=0.25;
endif
endif

calculateld:=L_d;
end

“Function to evaluate two phase flow length in sub-section E”

function calculatele(Q_sub, Q_TS)
L_sub=Q_sub/Q_TS*1.738;
if (L_sub>(0.167+1.25)) then
L_e=0.0001;
else
if (L_sub>(0.167+1.25)) then
L_e=0.25-(L_sub-(0.167+1.25));
else
L_e=0.25;
endif
endif

calculatele:=L_e;
end
"Geometric parameters"

\[ r_{in} = 6.23 \times 10^{-3} \]
\[ d_{tube} = r_{in} \times 2 \]
\[ r_{out} = 9.53 \times 10^{-3} \]
\[ A_{tube} = \pi r_{in}^2 \]
\[ k_{tube} = \frac{340}{1000} \]
\[ \theta = 0 \]
\[ a_g = 9.81; \] "acceleration due to gravity"

\[ P_{crit} = P_{crit}(ref$) \]
\[ M = \text{molarmass}(ref$) \]
\[ ref$ = 'r134a' \] "refrigerant name is attached to a string"

"R134a mass flux"

\[ m_{ref} = m_{ref1}/60; \]
\[ G = m_{ref}/A_{tube}; \]
\[ G_{ref\_unc} = \text{uncertaintyof}(G); \]

"Enthalpy at test section inlet"

\[ Q_{PH} = V1_{PH} \times I1_{PH}/1000; \]
\[ P_{TS\_avg} = (P1_{TS\_In} + P2_{TS\_Out})/2; \]
\[ P_{loss} = (P1_{TS\_In} - P2_{TS\_Out})/1.8; \]
\[ P_{cond\_avg} = (P3_{cond\_In} + P4_{cond\_Out})/2; \]
\[ i_{TS\_In} = \text{enthalpy}(ref$, P = P_{TS\_avg}, T = T103_{TS\_In}); \]
\[ T_{sat\_TS} = T_{sat}(ref$, P = P_{TS\_avg}); \]
\[ i_{f\_TS} = \text{enthalpy}(ref$, P = P_{TS\_avg}, x = 0); \]
\[ i_{g\_TS} = \text{enthalpy}(ref$, P = P_{TS\_avg}, x = 1); \]
\[ i_{fg\_TS} = i_{g\_TS} - i_{f\_TS}; \]
\[ Q_{sub} = m_{ref} \times (i_{f\_TS} - i_{TS\_In}); \]
\[ Q_{TS} = (V1_{PH} \times I1_{PH}/1000) + (V2_{TS} \times I2_{TS}/1000); \]
\[ L_a = \text{calcutlatea}(Q_{sub}, Q_{TS}); \]
\[ L_b = \text{calcutatelb}(Q_{sub}, Q_{TS}); \]
L_c=calculatelc(Q_sub, Q_TS);
L_d=calculateld(Q_sub, Q_TS);
L_e=calculatele(Q_sub, Q_TS);
L_f=0.25;

"Predicting density"
 rho_r134a=density(r134a, T=T103_TS_In, P=P1_TS_In);
 rho_rl22h=995;  "at 20 C"
 rho_zno= 5610;

mf_ref_base=0.98;
mf_oil_base=0.02;

vol_base=mf_ref_base/rho_r134a+mf_oil_base/rho_rl22h
 den_base=1/vol_base;

mf_r134a=0.9668;
mf_rl22h=0.0198;
mf_zno=0.0134;

vol_mix=mf_r134a/rho_r134a+mf_rl22h/rho_rl22h+mf_zno/rho_zno;
 den_mix=1/vol_mix;

"Enthalpy at various TC locations and exit of test section"
i_1=i_TS_In+Q_TS/m_ref*0.167/1.738;
i_2=i_1+Q_TS/m_ref*0.25/1.738;
i_3=i_2+Q_TS/m_ref*0.25/1.738;
i_4=i_3+Q_TS/m_ref*0.25/1.738;
i_5=i_4+Q_TS/m_ref*0.25/1.738;
i_6=i_5+Q_TS/m_ref*0.25/1.738;
i_7=i_6+Q_TS/m_ref*0.25/1.738;
\[ i_{8} = i_{7} + Q_{TS}/m_{ref} \times 0.071/1.738; \]
\[ i_{TS\_exit} = i_{TS\_in} + Q_{TS}/m_{ref}; \]

"Quality at various TC locations and exit of test section"
\[ X_{in} = \text{qualityref}(i_{TS\_in}, i_{f\_TS}, i_{g\_TS}, P_{TS\_avg}); \]
\[ X_{1} = \text{qualityref}(i_{1}, i_{f\_TS}, i_{g\_TS}, P_{TS\_avg}); \]
\[ X_{2} = \text{qualityref}(i_{2}, i_{f\_TS}, i_{g\_TS}, P_{TS\_avg}); \]
\[ X_{3} = \text{qualityref}(i_{3}, i_{f\_TS}, i_{g\_TS}, P_{TS\_avg}); \]
\[ X_{4} = \text{qualityref}(i_{4}, i_{f\_TS}, i_{g\_TS}, P_{TS\_avg}); \]
\[ X_{5} = \text{qualityref}(i_{5}, i_{f\_TS}, i_{g\_TS}, P_{TS\_avg}); \]
\[ X_{6} = \text{qualityref}(i_{6}, i_{f\_TS}, i_{g\_TS}, P_{TS\_avg}); \]
\[ X_{7} = \text{qualityref}(i_{7}, i_{f\_TS}, i_{g\_TS}, P_{TS\_avg}); \]
\[ X_{exit} = \text{qualityref}(i_{TS\_exit}, i_{f\_TS}, i_{g\_TS}, P_{TS\_avg}); \]
\[ X_{exit\_unc} = \text{uncertaintyof}(X_{exit}); \]

"Average quality, pressure and temp in test section divisions"
\[ X_{avg\_1} = (X_{in} + X_{1})/2; \]
\[ X_{avg\_a} = (X_{1} + X_{2})/2; \]
\[ X_{avg\_b} = (X_{2} + X_{3})/2; \]
\[ X_{avg\_c} = (X_{3} + X_{4})/2; \]
\[ X_{avg\_d} = (X_{4} + X_{5})/2; \]
\[ X_{avg\_e} = (X_{5} + X_{6})/2; \]
\[ X_{avg\_f} = (X_{6} + X_{7})/2; \]
\[ X_{avg\_8} = (X_{7} + X_{exit})/2; \]
\[ X_{avg} = (X_{in} + X_{exit})/2; \]
\[ i_{avg\_1} = (i_{TS\_in} + i_{1})/2; \]
\[ i_{avg\_a} = (i_{1} + i_{2})/2; \]
\[ i_{avg\_b} = (i_{2} + i_{3})/2; \]
i_avg_c=(i_3+i_4)/2;
i_avg_d=(i_4+i_5)/2;
i_avg_e=(i_5+i_6)/2;
i_avg_f=(i_6+i_7)/2;
i_avg_8=(i_7+i_TS_exit)/2;
i_avg=(i_TS_in+i_TS_exit)/2;

T_avg_1=temperature(ref$, h=i_avg_1, P=P_TS_avg);
T_avg_a=temperature(ref$, h=i_avg_a, P=P_TS_avg);
T_avg_b=temperature(ref$, h=i_avg_b, P=P_TS_avg);
T_avg_c=temperature(ref$, h=i_avg_c, P=P_TS_avg);
T_avg_d=temperature(ref$, h=i_avg_d, P=P_TS_avg);
T_avg_e=temperature(ref$, h=i_avg_e, P=P_TS_avg);
T_avg_f=temperature(ref$, h=i_avg_f, P=P_TS_avg);
T_avg_8=temperature(ref$, h=i_avg_8, P=P_TS_avg);
T_avg=temperature(ref$, h=i_avg, P=P_TS_avg);

"Average convection coefficient in different sections"
T_w_avg_a=average(T215_TS1_Up, T214_TS1.Down, T212_TS2.Up); "T213_TS2.Down not working"
T_w_avg_b=average(T212_TS2.Up, T210_TS3.Up, T211_TS3.Down); "T213_TS2.Down not working"
T_w_avg=average(T_w_avg_a, T_w_avg_b, T_w_avg_c, T_w_avg_d, T_w_avg_e, T_w_avg_f);

Q_a=Q_TS*L_a/1.738;
\[Q_b = \frac{Q_{TS} \cdot L_b}{1.738} ;\]
\[Q_c = \frac{Q_{TS} \cdot L_c}{1.738} ;\]
\[Q_d = \frac{Q_{TS} \cdot L_d}{1.738} ;\]
\[Q_e = \frac{Q_{TS} \cdot L_e}{1.738} ;\]
\[Q_f = \frac{Q_{TS} \cdot L_f}{1.738} ;\]

\[h_{avg\_a1} = \frac{k_{tube} \cdot Q_a}{(r_{in} \cdot 2\pi \cdot L_a \cdot k_{tube} \cdot (T_{w\_avg\_a} - T_{avg\_a}) - Q_a \cdot \ln((r_{out} - 0.5e^-3)/r_{in}))};\]
\[h_{avg\_a} = if(L_a, 0.0001, 0, 0, h_{avg\_a1});\]
\[h_{avg\_b1} = \frac{k_{tube} \cdot Q_b}{(r_{in} \cdot 2\pi \cdot L_b \cdot k_{tube} \cdot (T_{w\_avg\_b} - T_{avg\_b}) - Q_b \cdot \ln((r_{out} - 0.5e^-3)/r_{in}))};\]
\[h_{avg\_b} = if(L_b, 0.0001, 0, 0, h_{avg\_b1});\]
\[h_{avg\_c1} = \frac{k_{tube} \cdot Q_c}{(r_{in} \cdot 2\pi \cdot L_c \cdot k_{tube} \cdot (T_{w\_avg\_c} - T_{avg\_c}) - Q_c \cdot \ln((r_{out} - 0.5e^-3)/r_{in}))};\]
\[h_{avg\_c} = if(L_c, 0.0001, 0, 0, h_{avg\_c1});\]
\[h_{avg\_d1} = \frac{k_{tube} \cdot Q_d}{(r_{in} \cdot 2\pi \cdot L_d \cdot k_{tube} \cdot (T_{w\_avg\_d} - T_{avg\_d}) - Q_d \cdot \ln((r_{out} - 0.5e^-3)/r_{in}))};\]
\[h_{avg\_d} = if(L_d, 0.0001, 0, 0, h_{avg\_d1});\]
\[h_{avg\_e1} = \frac{k_{tube} \cdot Q_e}{(r_{in} \cdot 2\pi \cdot L_e \cdot k_{tube} \cdot (T_{w\_avg\_e} - T_{avg\_e}) - Q_e \cdot \ln((r_{out} - 0.5e^-3)/r_{in}))};\]
\[h_{avg\_e} = if(L_e, 0.0001, 0, 0, h_{avg\_e1});\]
\[h_{avg\_f} = \frac{k_{tube} \cdot Q_f}{(r_{in} \cdot 2\pi \cdot L_f \cdot k_{tube} \cdot (T_{w\_avg\_f} - T_{avg\_f}) - Q_f \cdot \ln((r_{out} - 0.5e^-3)/r_{in}))};\]
\[h_{avg} = average(h_{avg\_a}, h_{avg\_b}, h_{avg\_c}, h_{avg\_d}, h_{avg\_e}, h_{avg\_f});\]
\[q\_flux = \frac{Q_{TS}}{2\pi r_{in} \cdot 1.738};\]
APPENDIX B: ADDITIONAL IMAGES FROM THE STUDY

Figure B.1: Pressure vessel with measurement devices (image courtesy of Berghof Inc.).
Figure B.2: Dispersion stability of a) CuO b) TiO2 nanoparticles in RL22H.
Figure B.3: a) Al$_2$O$_3$/RL22H dispersion with surface treatment 1 b) residue of the nanoparticles after stability test in R134a.
Figure B.4: a) Al₂O₃/RL22H dispersion with surface treatment 2 b) residue of the nanoparticles after stability test in R134a.
Figure B.5: a) Al₂O₃/RL22H dispersion with surface treatment 3 b) residue of the nanoparticles after stability test in R134a.
Figure B.6: a) Al$_2$O$_3$/RL22H dispersion with surface treatment 4 b) residue of the nanoparticles after stability test in R134a.
Figure B.7: a) Al₂O₃/RL22H dispersion with surface treatment 5 b) residue of the nanoparticles after stability test in R134a.