“NANO-REFRIGERATOR FOR ECO-FRIENDLY AND CLEAN ENVIRONMENT”

PROJECT REPORT

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CHAPTER 1

INTRODUCTION

1.1. REFRIGERATION

Refrigeration may be defined as the process of achieving and maintaining a temperature below that of the surroundings, the aim being to cool some product or space to the required temperature. One of the most important applications of refrigeration has been the preservation of perishable food products by storing them at low temperatures. Refrigeration systems are also used extensively for providing thermal comfort to human beings by means of air conditioning.

1.2 INDIAN SCENARIO

The refrigeration and air conditioning sector in India has long history from the early years of last century. India is presently producing R134a, R22, R717 and hydro carbon based refrigeration and air conditioning units in large quantities. The use of CFC refrigerants in new systems was stopped since the year 2002. The factors that dictate the adoption of a particular refrigerant apart from its suitability for the specific application are its availability and cost. The halogenated refrigerants such as R12, R22, R134a and natural refrigerant like R717 are readily available at low prices. The Hydrocarbon (HC) and Hydro Fluro Carbon (HFC) mixtures (such as R404a, R407, and R410A) are not currently manufactured indigenously and hence have to be imported at a higher cost. This is likely to affect the growth in refrigeration and air conditioning sector in India and also the total conversion to environmental friendly alternatives in the near future.

1.3 DOMESTIC REFRIGERATION

The Indian household refrigerator industry is more than 50 years old. Eight major domestic refrigerator manufactures were catering this market, of which four are manufacturing hermetic compressors. Domestic refrigerators manufactured in India range in capacities from 65 to 580 l. Most of the currently produced Indian
refrigerators uses R134a as refrigerant. The choice of alternative to R134a is narrowed down to R152a and hydrocarbon refrigerants. Refrigerators manufactured before 2000 were still running on R12. To full fill the objectives of the Montreal Protocol, R12 has to be replaced by either hydrocarbon mixtures or R134a/hydrocarbon mixtures without modification in the existing system.

1.4 COMMERCIAL AND INDUSTRIAL REFRIGERATION

Most of commercial freezers like chest freezers, bottle coolers, visi coolers, display cabinets, water coolers and walk in coolers are using R134a and R12 as the refrigerant. Annual production of commercial refrigerated cabins (such as chest freezers, display cabinets, bottle coolers and visi coolers), water coolers and walk in coolers in India were estimated to be about 40,000, 27000, and 500 units respectively. About 80% of these units are manufactured by small and medium enterprises (Ministry of Environment and Forest, 2005). The choice of suitable alternative to R134a in commercial applications is R152a and hydrocarbon mixtures. The estimated population of milk chilling and cold storage in India was about 14,000. Most of the cold storage and milk chilling plants are working on ammonia and some on R502. Ammonia will dominate the industrial refrigeration sector due to its favorable environment properties (zero ODP and GWP). The alternative choice for R502 is 507 and hydrocarbon mixtures for low temperature industrial applications.

1.5 AIR CONDITIONERS, HEAT PUMPS AND CHILLERS

In India it is estimated that one million room air conditioners is being manufactured with R22 as refrigerant every year, which compromises of window, split and packaged air conditioning units (Devotta et al., 2005). The capacity of the windows air conditioners ranges from 0.5 TR to 2 TR. The choice of alternative to R22 in air conditioning applications is R407 and R410 which are available in the Indian market. Annually about 4000 central air conditioning chillers were installed, most of these chillers was based on R22 and R11. Very limited chillers were presently installed with R123 due to the lack of availability on this refrigerant. The long – term alternative to R11 and R22 for the chiller applications is R123.
1.6 AUTOMOBILE AIR CONDITIONERS

Three manufactures in India are producing about 50,000 units of automobile air conditioners annually. Most of these units are R134a based system. The choice of alternative to R134a is R152a and hydrocarbon mixtures. The car air conditioning units installed before 2000 were still running on R12 only. The choice of alternative to R12 and R134a is the mixture composed of R134a with hydrocarbon mixture or hydrocarbon mixtures and R152a.

Table 1.1 Future options in refrigerants

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Application</th>
<th>Future options</th>
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<tr>
<td>Refrigerator</td>
<td>Household (domestic)</td>
<td>HC mixtures, R152a</td>
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<td>Walk in coolers</td>
<td>Commercial</td>
<td>HC mixtures, R134a/ HC mixtures, R152a</td>
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<tr>
<td>Chest Freezer</td>
<td>Commercial</td>
<td>HC mixtures, R152a</td>
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<td>Air conditioners</td>
<td>Residential and Commercial</td>
<td>R290, R407C, R410A, R407C/ HC mixtures, R152a HC mixtures</td>
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<tr>
<td></td>
<td>Automobile</td>
<td>R123</td>
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<td></td>
<td>Industrial</td>
<td>Ammonia</td>
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<td>Chillers</td>
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<td>Cold Storage</td>
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The halogenated refrigerants like R22, R134a, R123, R404A, R407C, R410A and 507 will continue to be dominating during the next decade due to its high efficiency, safety and their current strong position in the Indian market. The Technologies identified for manufacturing new products in this sector are listed in table 1.1.
1.7 ENVIRONMENTAL IMPACTS

Green House gas (GHG) emissions from fossil fuel combustion for power generation and emission of halogenated refrigerants from vapour compression based refrigeration, air conditioning and heat pump systems contribute significantly to global warming. A reduction in GHG emissions can only be achieved by using environment friendly and energy efficient refrigerants. The high environmental impacts due to halogenated refrigerant emissions lead to identifying a long-term alternative to meet all the system requirements including system performance, refrigerant –lubricant interaction, energy efficiency, safety and service. Halogenated refrigerants are extensively used in the refrigeration and air conditioning industries over many decades due to their excellent thermodynamic and thermo-physical properties. As per the Montreal Protocol 1987, developing countries like India, with a per capita consumption less than 0.3 kg of ozone depletion substance have been categorized as Article-5 countries. These countries are required to phase out all Chloro Fluro carbons (CFCs) by 2010 and all hydro Chloro Fluro carbons (HCFCs) by 2040. HFC refrigerants are considered as one among the six targeted green house gas under Kyoto protocol of United Nations Framework Convention on Climate Change (UNFCCC) in 1997.

1.8 OZONE LAYER DEPLETION

The first major environmental impact that struck the refrigeration based industries is Ozone Depletion Potential (ODP) due to manmade chemicals into the atmosphere. About 90% of the ozone exists in the stratosphere between 10 and 50 km above the earth surface. Molena and Rowland (1974) give in detail that chlorine based refrigerants are stable enough to reach the stratosphere, where the chlorine atoms act as catalyst to destroy the stratospheric ozone layer which protects the earth surface from direct ultra violet rays.
1.9 GLOBAL WARMING POTENTIAL (GWP)

The second major environmental impact is GWP, which is due to the absorption of infrared emissions from the earth, causing an increase in global earth surface temperature. While solar radiation at 5800 K and 1360 W/m$^2$ arrives the earth, more than 30% is reflected back into space and most of the remaining radiation passes through the atmosphere and reaches the ground. This solar radiation heats up the earth, which is approximately as a black body radiating energy with a spectral peak in the infrared wavelength range. This infrared radiation cannot pass through the atmosphere because of absorption by GHG including the halogenated refrigerants.

1.10 NANO FLUIDS

Nanofluids are engineered colloids which consist of a base fluid with Nano sized particles (1-100 nm) suspended within them. Common base fluids include water, organic liquids (e.g. ethylene, tri-ethylene-glycols, refrigerants, etc.), oils and lubricants, bio-fluids, polymeric solutions and other common liquids. Materials commonly used as nanoparticles include chemically stable metals (e.g., gold, copper), metal oxides (alumina, silica, zirconia, Titania), oxide ceramics (e.g. Al$_2$O$_3$, CuO), metal carbides (e.g. SiC), metal nitrides (e.g. AlN, SiN), carbon in various forms (e.g., diamond, graphite, carbon nano tubes, fullerene) and functionalized nanoparticles. By suspending nanoparticles in conventional heat transfer fluids, the heat transfer performance of the fluids can be significantly improved. As a fluid class, Nanofluids have a unique feature which is quite different from those of conventional solid-liquid mixtures in which millimetre and/or micrometre-sized particles are added. Such particles settle rapidly, clog flow channels, erode pipelines and cause severe pressure drops. All these shortcomings prohibit the application of conventional solid-liquid mixtures to micro channels while nano fluids instead can be used in micro-scale heat transfer. Heat transfer performance of the nano fluid is superior to that of the original pure fluid because the suspended ultrafine particles remarkably increase the thermal conductivity of the mixture and improve its capability of energy exchange.
According to the application, nano fluids are classified as heat transfer nano fluids, tribological nano fluids, surfactant and coating nano fluids, chemical nano fluids, process/extraction nano fluids, environmental (pollution cleaning) nano fluids, bio- and pharmaceutical nano fluids and medical nano fluids (drug delivery, functional and tissue-cell interaction).

1.11 OBJECTIVES AND SCOPE OF THE PRESENT STUDY

Several investigations have been carried out to tackle the problem of Global Warming and Ozone layer depletion with the usage of alternative refrigerants in the refrigeration system. Hence it is felt that a detailed investigation on the possibility of exploring an new alternative refrigerant and addition of nano additives to the refrigerant and studying the effect of surfactant would be a worthwhile attempt. Accordingly the specific objectives of the present research work comprises of which are as follows:

- The most commonly used commercial refrigerant R134a and the proven alternative R152a were blended and the new hybrid refrigerant was prepared and the corresponding performance was investigated.
- Nano additives such as ZnO, CuO and Al$_2$O$_3$ were blended with R152a refrigerant and their corresponding performance on the same system was investigated. Nano additives of Al$_2$O$_3$, CuO and ZnO of 0.05%v, 0.1%v and 0.15%v concentration with particle size of 40-50 nm and 150 gm of R152a was charged and tests were conducted. The compressor discharge temperature, discharge pressure and evaporator temperature, Coefficient of performance (COP), vapour pressure, volumetric cooling capacity (VCC) were measured. An experimental test rig is designed and fabricated indigenously in the lab to carry out the investigations. Nanoparticles with refrigerant mixture were used in HFC R152a refrigeration system. The system performance with nanoparticles was then investigated.
- The effect of surfactant on the system performance was investigated. Two types of surfactants Sodium dodecyl sulfate (SDS) anionic surfactant and Cetyl tri methyl ammonium bromide (CTAB) cationic surfactant were added to the
compressor oil at their Critical Micelle Concentration (CMC) values and the system performance was investigated.

The scope of this work is limited based on the following

1. Three types of nano additives namely Al₂O₃, CuO and ZnO were selected for study.
2. The blending ratio of R134a and R152a were chosen as 30:70, 50:50, and 70:30 in this study
3. The concentration of nano additives were chosen as 0.05%v, 0.1 % v and 0.15%v in this investigation.
4. Only two surfactants viz. sodium dodecyl sulfate (SDS) an Cetyl tri methyl ammonium bromide (CTAB) representing anionic and cationic class of surfactants respectively have been employed in this investigation

1.12 ORGANIZATION OF THESIS

This thesis contains nine chapters with and introduction to the problem in first chapter followed by objectives and scope of the present study. In chapter 2, a comprehensive literature review on refrigeration, blending of refrigerants, addition of Nano additives in refrigeration system and the influence of the surfactants on the performance of the system are presented. The materials and methods including the refrigeration system, its types and the lubricant used in the refrigeration system were presented in chapter 3, chapter 4 presents the details of a Nanoparticles and the surfactants along with their properties. In chapter 5 the fabricating of the experimental setup along with synthesis of Nano fluids are presented. Chapter 6 presents the study on blending of R152a and R134a along with their results and discussion. In chapter 7 a detailed experimental study on the performance of nano additives in R152a refrigeration system was carried out. The effect of surfactants on the system performance was discussed in chapter 8.
Conclusions and the scope for future research work are highlighted in chapter 9. The overall outline of the present research study is presented in Fig. 1.1
Fig. 1.1 Outline of research study on nanoadditive and surfactants in refrigeration
CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Air conditioners and refrigerator-freezers are major energy users in a household environment and hence efficiency improvement of these appliances can be considered as an important step to reduce their energy consumption along with the environmental pollution prevention. Energy efficiency standards and labels are commonly used tools to reduce the energy uses for household appliances for many countries around the world.

The refrigeration sector is the midst of an unprecedented transition crisis catalysed by environmental concerns with the impact of the refrigerant emissions. As per the Montreal Protocol, CFC12 is being phased out following a stipulated time frame. The developed countries have already phased out this substances and the developing countries are to totally phase out the CFCs by 2010 as per the Montreal Protocol. Most of the developing countries are drastically reducing their CFC production and consumption. This demand for a suitable substitute for CFC12 for possible retrofitting of existing systems as well as for new systems.

The refrigerator production and sales rate in developing countries made significant leaps only in the last decade and for another 15 years all the refrigerators sold would one way or other come for service. Due to the reduction in production of CFCs and non availability and high cost of CFC refrigerants, the existing CFC based refrigerators (in India approximately 25 million) may have to be dispensed with as and when some service problems arise, which the economy of a developing country would not permit. To retrofit the existing CFC12 refrigerators with eco friendly technology two matching refrigerants are available, namely, HFC134a and HC blend. HFC134a systems do have inherent service issues because of the POE oil in the compressor, as HFC134a is not miscible with conventional mineral oil. On the other hand, HC blends have the problems of flammability and limitation in the charge
quantity due to safety (fire hazard) regulations. Hence, it would be a significant benefit for the RAC technicians in the service sector if HFC 134a can be made to work with mineral oil. It has been reported that the oil miscibility problem for HFC134a in mineral oil could be solved by adding suitable quantity of HC additive. (S. Joseph Sekhar et al. 2004)

2.2 BLENDING OF REFRIGERANTS

The environmental concerns with the impact of refrigerant emissions lead to the importance in identifying a long-term alternative to meet all requirements in respect of system performance and service.

Mao-Gang – He et al. (2005) used a mixture of HFC152a/HFC125 as refrigerant for domestic refrigerator and the performance was analysed. The results indicate the HFC152a/HFC125 mixture in the composition of 0.85 mass fraction of HFC152a as similar performance with the existing refrigerant CFC12. Experimental research on the main refrigeration performances of domestic refrigerators was conducted, under the different proportions and charge amounts, when HFC125a/AFC125 is used to substitute CFC12 as a “drop-in” refrigerant. The experimental results indicate that the refrigeration performances of the domestic refrigerator charged with the new refrigerant can meet the requirement of the National Standard of China, under the appropriate proportion and the optimum charge amount. The optimum charge amount that determine based on the energy consumption and the main operating parameters the precision of the charged amount was ±1g. The purity used in their analyses was not lower than 99.5%. In the mass proportion HFC152a/HFC125 is 15.13/84.87 wt% and the charge amount is 97g, the energy consumption is lowest as 1.156 kW/h/per day. They concluded that the mixing refrigerant HFC152a/HFC125 proposed in their study is a long term alternative to CFC12.
M.S. Kim et al. (1994) conducted a performance evaluation of two azeotropic refrigerant mixtures of HFC134a with HC290 and HC600a on heat pump and established that COP of the CFC12 heat pumps improved by 3.5% when they were retrofitted with a mixture of HFC134a/HC600a (80:20) by weight.

D.Jung et al. (1996) tested the hydrocarbon mixture of HC290/HC600a mixture at various composition on a domestic refrigerator at various composition and found that with 0.55-0.6 mass percentage of HC600a yielded 3 - 4% increase in energy efficiency as compared to CFC12.

Miguel Padilla et al. (2010) studied the energy analysis of the impact of direct replacement of R12 with the zeotropic mixture R413a on the performance of a domestic vapour compression refrigeration system. They found that the evaporator outlet temperature ranged from 15°C to -10°C. The overall energy performance of the system working with R413a is consistently better than that of R12.

Alka Bani Agarwal and Vipin Shrivastava (2010) retrofitted a vapour compression refrigeration trainer by an eco-friendly refrigerant. After year’s successful deliberations for tackling the grievous problem of ozone depletion, the United Nation’s environmental protection agency concluded multinational agreement called “Monteral Protocol” for controlling the use of gases threatening the ozone layer. The successful implementation of the “Monteral Protocol” in developed countries is being appreciated for its significant reduction in emission level of ozone depleting substances. Now it is turn of developing countries to fulfill their obligation of Montreal Protocol. The dead line for complying with the phase out of Chlorofluro carbon in developing countries like India is 2010. The refrigeration industry has accepted the challenge of chloroflourocarbons phase out and new eco-friendly refrigerant like hydrofluorocarbons and hydrocarbons are replacing chloroflourocarbons in all commercial and industrial application. Vapour compression refrigeration trainer is an important equipment of thermal engineering lab of mechanical engineering department which operated using chloroflurocarbon 12. CFC12 is the most important member of CFC refrigerants which are being targeted for phase out in India by 2010. Performance valuation of many eco-friendly hydrocarbon refrigerants for replacing CFC12 in the
trainer has been done and a suitable drop in alternative refrigerant for retrofitted has been identified.

Zhijing Liu et al. (2012) tested R290/R600 mixture as a drop-in substitute in a 20-cubic feet, single-evaporator, auto defrost, top mount, conventional domestic refrigerator/freezer. All the hardware remained the same, only the capillary tube was lengthened to achieve the optimum performance. The best result with an optimized R290/R600 blend was 6% savings compared to the baseline test with R12. In the second part of the research, an 18.0 cubic-feet, auto defrost, top mount, domestic refrigerator was used for experiments. Having tested for the single-evaporator baseline performance, the unit was converted to a two-evaporator modified Lorenz-Meutzner cycle. The optimum performance of the modified unit yield 14.6% and 16.7% energy savings with binary mixtures R290/nc5, and R290/R600, respectively. A ternary mixture R290/R600/nc5 with 17.3% energy savings proved to be better than the binary mixtures. The superior transport properties of the hydrocarbon mixture are believed to be responsible for their better test performance.

A.S. Dalkilic and S. Wongwises (2010) made a performance comparison of vapour-compression refrigeration system using various alternative refrigerants. A theoretical performance study on a traditional vapour-compression refrigeration system with refrigerant mixtures based on HFC134a, HFC152a, HFC32, HC290, HC1270, Hc600, and HC600a was done for various ratios and their results are compared with CFC12, CFC22 and HFC134a as possible alternative replacements.

Abhishek Tiwari et al. (2011) conducted on experimental study of R404a and R134a, environment-friendly refrigerants with zero ozone depletion potential (ODP) and low global warming potential (GWP), to replace R134a in domestic refrigerator. A refrigerator designed and developed to work with R134a was tested, and its performance using R404a was evaluated and compared with its performance when R134a was used. The results obtained showed that the design temperature and pull-down time set by International Standard Organization (ISO) for small refrigerator were achieved earlier using refrigerant R-401a than using R-134a. The system consumed
less energy when R134a was used. The performance of R404a in the domestic refrigerator was constantly better than those of R134a throughout all the operating conditions, which shows that R404a can be used as replacement for R134a in domestic refrigerator.

M. Mohanraj et al. (2009) conducted an experimental investigation with hydrocarbon refrigerant mixture (composed of R290 and R600a in the ratio of 45.2:54.8 by weight) as an alternative to R134a in a 2001 single evaporator domestic refrigerator. Continuous running tests were performed under different ambient temperatures (24, 28, 32, 38 and 43°C), while cycling running (ON/OFF) tests were carried out only at 32°C ambient temperature. The results showed that the hydrocarbon mixture has lower values of energy consumption; pull down time and ON time ratio by about 11.1%, 11.6% and 13.2% respectively with 3.25-3.6% higher coefficient of performance (COP). The above hydrocarbons refrigerant mixture could be the best long term alternative to phase out R134a.

B.O. Bolaji et al. (2011) analaysed the performances of the three ozone Hydro fluorocarbon (HFC) refrigerants (R32, R134a and R512a) in a vapour compression refrigeration system were investigated experimentally and compared. The results obtained showed that R32 yielded undesirable characteristics, such as high pressure and low co-efficient of performance (COP). Comparison among the investigated refrigerants confirmed that R152a and R134a have approximately the same performance, but the best performance was obtained from the used of R152a in the system. As a result, R152a could be used as a drop-in replacement for R134a in vapour compression refrigerant system. The COP of R152a obtained was higher than those of R134a and R32 by 2.5% and 14.7% respectively. Also, R152a offers the best desirable environmental requirements; zero ozone potential and very low global warming potential.

S. Joseph Sekhar et al. (2004) presented two potential substitutes, namely, HFC134a and HC blends are available as drop in substitutes for CFC12. HC (hydrocarbon) refrigerants do have inherent problems in respect flammability. HFC134a is neither flammable nor toxic. But HFCs (hydro fluorocarbons) are not
compatible with mineral oil and the oil change is a major issue while retrofitting. The above techno-economic feasibility issue to retrofit the existing CFC12 systems with ozone friendly refrigerant and the energy efficiency of the system are the challenges in the domestic refrigeration sector. They carried out an experimental analysis in a 165 litre CFC12 household refrigerator retrofitted with eco-friendly refrigerant mixture HFC134a/HC290/HC600a without changing the mineral oil. Its performance, as well as energy consumption, is compared with the conventional one. As the system has been running successfully for more than 12 months consumption by 4 to 11% and improve the actual COP by 3 to 8% from that of CFC12. The new mixture also showed 3 to 12% improvement in theoretical COP. The overall performance has proved that the new mixture could be an eco-friendly substitute to phase out CFC12.

Ching-Song Jwo et al. (2009) investigated to apply the mixture of hydrocarbon refrigerants, R290 and R-600a with each 50% component ratio, instead of the refrigerant R134a for home refrigerators. The hydrocarbon refrigerants of R290 and R600a are friendly for environmental protection and have good refrigerating behavior in comparison with CFCs, HVFs or HFCs refrigerants. The experiments used a 440 litre capacity home refrigerator as test facility, which officially works with 150g R134a refrigerant was replaced by varied mass hydrocarbon refrigerant, which was mixed by R290 and R600a with each 50% component ratio. The results show that refrigerating effect is improved by using hydrocarbon refrigerant. Moreover, the total consumed energy is saved 4.4% and applied mass of refrigerant is reduced 40%.

2.2.1 Technical difficulties of mixed alternatives

The technical difficulties of the alternative refrigerant mixtures are listed below:

(a) The major problem of the refrigerant mixtures is the occurrence of pinch points in the condensers and evaporators during phase change due to non-linear variation in refrigerant properties, which reduces condenser and evaporation effectiveness (Venkatarathnam and Srinivasamoorthy, 1999).
(b) Non-isothermal behavior of the refrigerant mixtures creates ambiguity in selecting the components of the refrigeration system from the manufacture’s catalogue.

(c) Perfect glide matching can be achieved only in certain heat exchange geometries such as shell and tube, concentric tubes, counter flow and flat plate heat exchangers.

(d) Conventional method of heat exchangers design is not fully valid for the case mixed refrigerants (Rajaoaksha, 2007)

(e) Non-linearity of the mixtures influences to decreasing the temperature difference at inlet and outlet may lead to increase in heat exchanger area to achieve the desired capacity.

(f) Composition shift due to leakage of refrigerant of the mixed refrigerants leads to change in pressure, temperature, capacity and efficiency (Johansson and Lundqrist, 2001)

(g) Mixed refrigerants require liquid receiver and suction line accumulator due to composition variation in phase change (Rajapaksha and Suen, 2004)

2.3 NANO FLUIDS

2.3.1 Historical overview

It is well known fact that conventional fluids such as water, ethylene glycol (EG) and engine oils have low thermal conductivity and the efficiency of heat transfer with a very small temperature difference is limited. There is a need for energy efficient working fluids to improve the energy conversion system. However the coefficient of convective heat transfer depends on thermal conductivity of the fluid. The thermal conductivity of fluid is improved by adding micrometer or millimeter sized solid materials to the base fluids. The solid additives improves the thermal conductivity of the base fluid. The practical applications are limited due to the clogging of flow channels, sedimentation of large particles and causing pressure drops. The above drawbacks are overwhelmed by using a new class of fluids called nanofluids. Choi in Argonne National Laboratory introduced the concept of nanofluids. Nanofluids are a new class of solid-liquid composite materials consisting of solid nanoparticles (in the
range of 1-100 nm) or carbon nano tubes, dispersed in a heat transfer fluid such as ethylene glycol, water or oil.

2.3.2 Techniques used in synthesis of nanofluids

Several researchers carried out the synthesis of nanofluids using two step and single step method. In case of two step method, the nanoparticles are produced initially and then it is added into the working fluid in case of single step method the dispersion of nanoparticle is done directly into the working fluid.

2.3.3 Synthesis of nanofluids using two step method

The preparation of nanofluids is done by mixing the nanoparticles directly into the base fluid. The nanoparticles are produced at first step and then it is added into the base fluid as a second step. Xuan and Li (2000) presented a procedure for preparing a nanofluid which is a suspension consisting of nano phase powders and a base liquid. Two different kinds of nanofluids are prepared by varying the base fluid. The first one is the transformer oil based nanofluid which is prepared by adding Cu nanoparticles by 2 and 5 vol% respectively and the suspension are stabilized with the oleic acid. The second is the preparation of water based copper nanofluid in which Cu nanoparticles are added by 5 vol% and laurate salt is added to stabilize the suspension.

Patel et al. (2003) measured the thermal conductivity of Au nanoparticles in water and toluene and the size of the nanoparticles used in this study is of 10-20 nm in diameter by adding citrate as the stabilization agent.

Putnam et al. (2006) prepared nanofluid which consisted the mixtures of C60–C70 fullerenes in toluene and alkanethiolate stabilized Au nanoparticles in ethanol and toluene by using two step processes for measuring thermal conductivity.
Murshed et al. (2005) prepared two kinds of nanofluids of which one is in spherical shaped TiO$_2$ nanoparticles of diameter 15 nm and the other one is rod shaped TiO$_2$ nanoparticles of 10 nm in diameter and 40 nm in length for comparing the thermal conductivity.

Wang et al. (1999) and Lee et al. (1999) measured the thermal conductivity of Al$_2$O$_3$ and CuO nanofluid which is prepared by two step method using different base fluids such as water, vacuum pump fluid, engine oil, and ethylene glycol. Experimental results show that the thermal conductivities of nanoparticle–fluid mixtures are higher than that of the base fluids.

Wang et al. (2006) prepared water– based multiwall carbon nanotube dispersed nanofluids using sodium dodecyl sulfate (SDS) dispersions, since the fibers are entangled in the aqueous suspension. However, the heat transfer performance of the nanofluids is affected by the addition of dispersions in fluids, especially at high temperature.

Hong et al. (2005) prepared Fe nanofluids with ethylene glycol using Fe nanocrystalline powder which is synthesized by a chemical vapour condensation process. To improve the suspension of the nanoparticles, sonication is carried out with high-powered pulses to improve the dispersion of nanoparticles in the preparation of nanofluids. After, sonication nanofluids exhibit an enhancement of thermal conductivity. Thermal conductivity of a Fe nanofluid is increased nonlinearly up to 18% as the volume fraction of particles is increased up to 0.55 Vol. %.

Liu et al. (2005) using a two-step method prepared CNT nanofluids using ethylene glycol and synthetic engine oil for measuring thermal conductivity of the nanofluids and the volume concentration of CNT–ethylene glycol suspensions is below 1.0 Vol. % and that of CNT–synthetic engine oil suspensions is below 2.0 Vol. %. Results indicate that the CNT–synthetic engine oil suspension has a much higher enhanced thermal conductivity ratio than that of the CNT–ethylene glycol suspension.
The two-step method for preparing nanofluids is a process by dispersing nanoparticles into base liquids. This step-by-step method isolates the preparation of the nanofluids from the preparation of nanoparticles. As a result, agglomeration of nanoparticles may take place in both steps, especially in the process of drying, storage, and transportation of nanoparticles. The agglomeration will not only result in the settlement and clogging of microchannels, but also decrease the thermal conductivity. Simple techniques such as ultrasonic agitation or the addition of surfactants to the fluids are often used to minimize particle aggregation and improve dispersion behavior. Since nanopowder synthesis techniques have already been scaled up to industrial production levels by several companies, there are potential economic advantages in using two-step synthesis methods that rely on the use of such powders. But an important problem that needs to be solved is the stabilization of the suspension prepared.

2.3.4 Synthesis of nanofluids using single step method

Eastman and Choi (2001) has used a one-step physical synthesis method to prepare nanofluids, in which Cu vapor was directly condensed into nanoparticles by contact with a flowing low vapor pressure liquid (ethylene glycol) and the effective thermal conductivity of ethylene glycol was shown to be increased up to 40% for a nanofluid consisting of ethylene glycol containing approximately 0.3 Vol% Cu nanoparticles of mean diameter, 10 nm.

Liu et al. (2006) used the technique of chemical reduction method for synthesis of nanofluids containing Cu nanoparticles in water without using surfactant as the dispersant. Thus the synthesized copper nanofluid shows improved thermal conductivity when compared to pure fluids.

Hong et al. (2005) employed chemical vapour condensation process to synthesis Fe nanofluids with ethylene glycol. The thermal conductivity of a Fe nanofluid is increased nonlinearly up to 18% as the volume fraction of particles is increased up to 0.55 Vol. %.
Lo et al. (2005) developed submerged arc nano synthesis system for preparing Cu-based nanofluids with different morphologies and using various dielectric liquids by selecting pure copper as an electrode as well as the work piece material. Also the advantage of this method is that allows the production of uniform and well-dispersed copper nanoparticles without any aggregation.

Zhu et al. (2004) presented a novel one-step chemical method for preparing copper nanofluids by reducing CuSO$_4$·5H$_2$O with NaH$_2$PO$_2$·H$_2$O in ethylene glycol under microwave irradiation. By this method non agglomerated and stably suspended Cu nanofluids were obtained. This method also found to be a fast and efficient for preparing Cu nanofluids.

The single-step method is a process of combining the preparation of nanoparticles with the synthesis of nanofluids, for which the nanoparticles are directly prepared by physical vapour deposition (PVD) technique or liquid chemical method. In this method the processes of drying, storage, transportation, and dispersion of nanoparticles are avoided, so the agglomeration of nanoparticles is minimized and the stability of fluids is increased. But a disadvantage of this method is that only low vapour pressure fluids are compatible with the process. This limits the application of the method.

2.3.5 Thermo physical properties of nanofluids

Habib Anifar et al. (2013) studied the Brownian and thermophoresis effects on natural convection of alumina-water nano fluid and found that heat transfer rate decreases with an increases in nanoparticle volume fraction.

Jahar Sarkar et al. (2013) studied the thermodynamic analysis and optimization of a two-stage cascade system with a choice of eight natural refrigerants. Their study reported two selection charts along with tables one for higher coefficient of performance and the other for highest volumetric capacity.
Aminfar et al. (2011) investigated the laminar flow and convective heat transfer of water – alumina nanofluid in a rectangular micro channel numerically. The results indicated that usage of nanofluid enhances convective heat transfer and pressure drop in a microchannel in comparison with pure water.

Liu et al. (2010) investigation discovered that the thermal performance of a mesh heat pipe can be evidently strengthened by substituting CuO nanofluids for deionized water under sub-atmospheric pressures.

Tsai et al. (2004) employed gold nanoparticles in nanofluid as working medium for conventional circular heat pipe and predicted the thermal resistance of the heat pipes with nanoparticle solution is lower than that with DI water.

Liu et al. (2011) performed an experimental work on the micro-grooved heat pipe using aqueous nanofluids as the working fluids and reported that addition of Cu and CuO nanoparticles in the base fluid can apparently improve the thermal performance of the heat pipe.

Misheck et al. (2006) studied the performance of heat pipe with coarse and fine pores wick structure. An improvement of heat pipe performance up to a factor of 2 was reported with such a type of wick.

Tsai et al. (2004) employed gold nanoparticles in nanofluid as working medium for conventional circular heat pipe and predicted the thermal resistance of the heat pipes with nanoparticle solution is lower than that with DI water.

2.3.6 Nano fluids for refrigeration

The nanofluid is a new type of heat transfer fluid by suspending nano-scale materials in a conventional host fluid and has higher thermal conductivity than the conventional host fluid. The nano refrigerant is one kind of nanofluid and its host fluid is a refrigerant. A nanorefrigerant has higher heat transfer coefficient than the host refrigerant and it can be used to improve the performance of the refrigeration systems. The heat transfer coefficient of a fluid with lower thermal conductivity is larger than that of a fluid with lower thermal conductivity if the Nusselt numbers of them are the same.
Therefore, researches on improving thermal conductivities of nanorefrigerants are necessary. There are two methods to improve the thermal conductivity of a nano refrigerant. The first one is to increase the volume fraction of nano scale materials in the nanorefrigerants and the second one is to use nano-scale materials with high thermal conductivity (Jiang et al. 2009).

Jiang et al. (2009) showed that the thermal conductivities of carbon nanotube (CNT) nanorefrigerants are much higher than those of CNT-water Nanofluids or spherical-nano particle-R113 nanorefrigerants. Authors reported that the smaller the diameter of CNT is or the larger the aspect ratio of CNT is the larger the thermal conductivity enhancement of CNT nano refrigerant.

Elcock (2007) found that TiO$_2$ nanoparticles can be used as additives to enhance the solubility of the mineral oil with hydro fluorocarbon (HFC) refrigerant. Authors also reported that refrigeration systems using a mixture of HFC134a and mineral oil with TiO$_2$ nano particles appear to give better performance by returning more lubricant oil to the compressor with similar performance to systems using HFC134a and POE oil.

Hindawi (2009) carried out an experimental study on the boiling heat transfer characteristics of R22 refrigerant with Al$_2$O$_3$ nano particles and found that the nanoparticles enhanced the refrigerant heat transfer characteristics with reduced bubble sizes.

Eastman et al. (1996) investigated the pool boiling heat transfer characteristics of R11 refrigerant with TiO$_2$ nano particles and showed that the heat transfer enhancement reached 20% at a particle loading of 0.01g/L.

Liu et al. (2006) investigated the effects of carbon nano tubes (CNTs) on the nucleate boiling heat transfer of R123 and HFC134a refrigerants. Authors reported that CNTs increase the nucleate boiling heat transfer coefficient for these refrigerants. Authors noticed large enhancements of up to 36.6% at low heat fluxes of less than 30kW/m$^2$. Thus, the use of nano particles in refrigeration systems is a new, innovative way to enhance the efficiency and reliability in the refrigeration system.
Bi et al. (2011) conducted an experimental study on the performance of a domestic refrigerator using TiO$_2$-R600a nanorefrigerant as working fluid. They showed that the TiO$_2$-R600a system worked normally and efficiently in the refrigerator and an energy saving 9.6%. They also reported freezing velocity of anno refrigerating system was more than that with pure R600a system.

N. Subramani et al. (2011) established that addition of nano particles to the refrigerant results in improvements in the thermo physical properties and heat transfer characteristics of the refrigerant, thereby improving the performance of the refrigeration system. Stable nano lubricant works has been prepared for their study. The experimental studies indicated that the refrigeration system with nano refrigerant works normally. It is found that the freezing capacity is higher and the power consumption reduces by 25% when POE oil is replaced by a mixture of mineral oil and alumina nano particles. Calculation shows that the enhancement factor in the evaporator is 1.53 when nano refrigerants are used instead of pure refrigerant.

Eed Abdel-Hafez-Hadi et al. (2011) studied the effect of using nano Cu-R134a in the vapour compression system on the evaporation heat transfer coefficient is experimentally investigated. An experimental test rig is designed and constructed here for this purpose. The test section is a horizontal tube in tube heat exchanger made from copper. The refrigerant is evaporated inside an inner copper tube and the heat load is provided from hot water that passing in an annulus surrounding the inner tube. Measurements were performed for heat flux ranged from 10 to 40 kW/m$^2$, using nano CuO concentration ranged from 0.05% to 1% and particle size from 15 to 70nm. The measurements indicated that for certain nano concentration as heat flux or mass flux increase the evaporating heat transfer coefficient increases. The measurements indicated also that the evaporating heat transfer coefficient increase with increasing nano CuO concentrations up to certain value then decreases.

R. Reji Kumar et al. (2013) investigated the heat transfer enhancement numerically on the surface of a refrigerator by using Al$_2$O$_3$ nano-refrigerants. The addition of anno particles to the refrigerant results in improvements in the thermophysical properties and heat transfer characteristics of the refrigerant, thereby improving the performance of the
refrigeration system. The experimental studies indicate that the refrigeration system with nano-refrigerant works normally. It is found that the freezing capacity is higher and the power consumption reduces by 11.5% when POE oil is replaced by a mixture of mineral oil and Aluminium oxide nano particles. Thus using Aluminium oxide nano-lubricant in refrigeration system is feasible.

R. Saidur et al. (2011) reviewed the thermal-physical properties of nanoparticles suspended in refrigerant and lubricating oil of refrigerating systems. Heat transfer performance of different nanorefrigerants with varying concentrations was reviewed and review results as presented as well. Pressure drop and pumping power of a refrigeration system with nanorefrigerants were obtained from different sources and reported in this review. Along with these, pool boiling heat transfer performance of CNT refrigerant was reported.

Moreover challenges and future direction of nanofluids/nanorefrigerants have been reviewed and presented in this paper. Based on result available in the literatures, it has been found that nanorefrigerants have much higher and strongly temperature-dependent thermal conductivity at very low particle concentrations than conventional refrigerant. This can be considered as one of the key parameters for enhanced performance for refrigeration and air conditioning systems.

The results indicate HFC134a and mineral oil with TiO$_2$ nano particles works normally and safely in the refrigerator with better performance. The energy consumption of the HFC134a refrigerant using mineral oil and nano particles mixture as lubricant saved 26.1% energy with 0.1% mass fraction TiO$_2$ nano particles compared to the HFC134a and POE oil system. It was identified that fundamental properties (i.e. density, specific heat capacity, and surface tension) or nano refrigerants were not experimentally determined yet. It may be noted as well that few barriers and challenges those have been identified in this review must be addressed carefully before it can be fully implemented in refrigeration and air conditioning system.
2.3.7 Advantages of nano fluids

- High specific surface area and therefore more heat transfer surface between particles and fluids
- High dispersion stability with predominant Brownian motion of particles.
- Reduced pumping power as compared to pure liquid to achieve equivalent heat transfer intensification.
- Reduced particle clogging as compared to conventional slurries, thus promoting system miniaturization.
- Adjustable properties, including thermal conductivity and surface wettability, by varying particle concentrations to suit different applications.

2.4 SURFACTANTS

Surfactants are surface active agents that lower the surface tension of a fluid, allowing spreading and lower the interfacial tension between two fluids. Surfactants are in organic compounds that are amphiphilic, meaning they contain both hydrophobic (their “tails”) and hydrophilic (their “heads”). Therefore both are soluble in both organic solvents and water. Surfactants reduce the surface tension of water by adsorption at the liquid-gas interface. Many surfactants can also assemble in the bulk solution into aggregates. Some of these aggregates are known as micelles. The concentration at which surfactants begin to form micells is known as the critical micelle concentration (CMC). A surfactant can be classified by the presence of formally charged groups in its head. A nonionic surfactant has no charge groups in its head. The head of an ionic surfactant carries a net charge. If the charge is negative, the surfactant is more specifically called anionic; is positive, it is called cationic (Calbo, 1992).

Liu Yang et al. (2011) prepared two types of nano fluids are obtained by adding the mixture of carbon black nano particles with emulsifier OP-10, and Al₂O₃ nano particles with sodium dodecyl benzene sulfonate SDBs in the ammonia-water solution, respectively. The dispersion stability of the prepared Nanofluids in different mass fractions of surfactants is investigated by the light absorbency ratio index methods. The results show that with the increase of mass fraction of surfactant, the stability of carbon
black nanofluid is improved firstly and then is exacerbated, while stability of Al$_2$O$_3$ nanofluid is exacerbated firstly, then is improved, and then is exacerbated again. The influences of surfactant on the stability of ammonia-water nanofluids abide by the monolayer adsorption theory or electric double layer adsorption theory. Finally, the theoretical surfactant mass fractions required in the preparation of ammonia water nano fluids are calculated by simplifying the dispersion models and the results are in accordance with experimental results.

Kim et al. (2006) defined binary nano fluid as the binary mixture in which nano particles were evenly distributed and the effect of binary nano fluid on the ammonia water bubble absorption performance was studied. It was found that, compared with ammonia-water, the absorption rate of ammonia- water nano fluid adding nano particles and the nano fluid adding both nano particles and surfactants was 3.21 times higher and 5.32 time higher respectively.

Michael S. Saterile et al. (2012) studied the power agglomeration and thermal conductivity in copper-based nanofluids. After careful determination of morphology and purity, they systematically and rigorously compared all three of the surfactants for the production of viable copper-based nano fluids during synthesis of copper nano powders has important consequences on the dispersion of the powders in a base fluid. The oleic-acid-prepared powders consisted of small particles of ~ 100nm that did not change with addition of dispersant. The CTAB prepared powders exhibited the best dispersion characteristics, as they formed small particles of approximately 80nm in the presence of SDBS. The thermal conductivity enhancement in nano fluids exhibited in linear relationship with powder loading for an average particle size of ~ 100nm and similar particle size distributions that range from ~50 to 650 nm, but independent of crystallite size and with all other factors maintained constant (surface area, surface additives, levels of oxidation) such that a 0.55 vol% loading results in a thermal conductivity enhancement of 22% over water and 1.0 vol% loading results in a thermal conductivity enhancement of 48% over water.

Saterlie M. S. et al. (2011) demonstrated that copper based Nanofluids the increase in thermal conductivity was due to the formation of controlled agglomeration.
Powders prepared using oleic acid and cetyl trimethyl ammonium bromide (CTAB) exhibited agglomeration when introduced in the base fluid, remained stable over extended period of time, and possessed enhancements of up to 48% for the case of the 1 vol % nano fluids of the CTAB-prepared powders. Specifically the powders in the base fluid had average particle size of ~120 and ~80 nm for the oleic acid and CTAB-prepared powders, respectively, at a particle loading of 0.55 vol %. When increasing the nano powder loading to 1.0 vol % the nano fluids of oleic acid prepared powders became heavily agglomerated, increasing the particle size from 120 to 800 nm and resulting in settling of the powders in the nano fluid. On the other hand, the nanofluids of the CTAB prepared powders were only slightly more agglomerated at the large powder loading, with a particle size average of 107 nm.

Hence based on the literature it is apparently clear that addition of different nano additives in refrigeration system improves the performance of the system. However only limited investigation has been carried out with nano additives in R152a refrigerant. Hence it is a worthwhile attempt to hybrid nano additives with R152a refrigerant in refrigerant system and also it will be useful to study the influence of surfactants on the performance of refrigeration system.

2.5 SUMMARY

In this chapter a review of the relevant literature on blending of refrigerants, addition of nanoparticles in refrigerants and the influence of the surfactants on the performance of the system were discussed. This forms the basis for defining the objective of the present investigation and also identifying the experimental procedures to be adopted to understand the role played by the surfactants with specific reference to dispersion and stability of nano fluids used in the refrigeration process. The detailed study on the refrigeration system and its types are carried out in the following chapter.
CHAPTER 3

REFRIGERATION SYSTEM

3.1 PROBLEM DEFINITION

The Global Warming Potential (GWP) of currently used R134a is high as 1300. The Ozone Depleting Potential (ODP) of R134a is also relatively high. The Montreal and Kyoto Protocol of United Nations suggests minimizing of Hydro Fluro carbons (HFCs) to use as refrigerants. Researches show HFC 134a not much miscible with lubricant oil in the compressor. European countries have already banned R134a. Blending of R134a with other HFC is a problem. R-22 and R134a will be phased out due to environmental issues. To overcome the above problem, refrigerant R152a is proposed in the present study because R152a has Zero Ozone Depleting Potential and a very less value of 120 as Global Warming Potential (GWP) when compared to other refrigerants. The atmospheric life span for R152a is 1.4 years. Pure substance R152a offers excellent thermodynamic properties non toxic and compatibility with the conventional oil in compressor. R152a has been already approved for use in automobile applications as an alternative to R134a by US Environmental Protection Agency.

3.2 REFRIGERATION PROCESS

3.2.1. Refrigerants

The working fluid used in the refrigeration system is termed as refrigerants. The mostly used Refrigerants now-a-days are a group of halogenated hydrocarbons, marketed under the various proprietary names of freon, genetron, arcton, isotron, frigen etc. These are either methane based or ethane based, where the hydrogen carbons are replaced by chlorine or fluorine atoms.
3.2.2. Working fluid – refrigerant

The mostly used Refrigerants now-a-days are a group of halogenated hydrocarbons, marketed under the various proprietary names of Freon, genetron, arcton, isotron, frigen etc. these are either methane based or ethane based, where the hydrogen carbons are replaced by chlorine or fluorine atoms.

It was realized in mid-seventies that the CFCs (chloro-fluoro carbons) not only allow more ultra violet radiation in to the earth’s atmosphere, but also prevents the infrared radiation from escaping the earth to outer space, which contributes to the greenhouse effect and hence, global warming. As a result, the use of some CFCs is banned (Montreal Protocol, 1987) and phased out on many countries. Fully halogenated CFCs (such as R-11, R12 and R115) do the most damage to the ozone depleting potential (ODP) of R-12. CFCs friendly to the ozone layer that protects the earth from ultraviolet rays and which do not contribute to the greenhouse effect are being developed. The chlorine free R-134a, a recent finding, is presently replacing R-12, the most widely used refrigerant, particularly in domestic refrigerators and freezers and automotive air conditioners.

3.2.3. Types of refrigeration systems

a. Vapour compression refrigeration systems,
   i. Domestic refrigeration systems
   ii. Air conditioning systems
b. Vapour absorption refrigeration systems
c. Solar energy based refrigeration systems
d. Air cycle refrigeration systems
e. Steam and vapour jet refrigeration systems
f. Thermoelectric refrigeration systems, and
g. Vortex tubes

Among the above most refrigeration system, most commonly used refrigeration is vapour compression refrigeration system.
3.2.4. Vapour compression refrigeration system

As mentioned, vapour compression refrigeration systems are the most commonly used among all refrigeration systems. As the name implies, these systems belong to the general class of vapour cycles, wherein the working fluid (refrigerant) undergoes phase change at least during one process. In a vapour compression refrigeration system, refrigeration is obtained as the refrigerant evaporates at low temperatures. The input to the system is in the form of mechanical energy required to run the compressor. Hence these systems are also called as mechanical refrigeration systems. Vapour compression refrigeration systems are available to suit almost all applications with the refrigeration capacities ranging from few Watts to few megawatts. A wide variety of refrigerants can be used in these systems to suit different applications, capacities etc. The actual vapour compression cycle is based on Evans-Perkins cycle, which is also called as reverse Rankine cycle. Before the actual cycle is discussed and analysed, it is essential to find the upper limit of performance of vapour compression cycles. This limit is set by a completely reversible cycle.

3.2.5 Components of vapour compression refrigeration system

There are four main components in vapour compression refrigeration system.

- Compressor
- Condenser
- Expansion valve
- Evaporator

3.2.6. Compressor

Compressors may be of three types:

- Reciprocating
- Rotary and
- Centrifugal
When the volume flow rate of the refrigerant is large, centrifugal compressors are used. Rotary compressors are used for small units. Reciprocating compressors are used in plants up to 100 tones capacity. For plants of higher capacities, centrifugal compressors are employed.

In reciprocating compressors, which may be single cylinder or multi cylinder ones, because of clearance, leakage past the pistons and valves, and throttling effects at the suction and discharge valves, the actual volume of gas drawn in to the cylinder is less than the volume displaced in the system.

3.2.7. Condenser

It must de superheat and then condense the compressed refrigerant. Condensers may be air cooled or water cooled. An air condenser is used in small units. Water cooled condensers are used in large installations.

3.2.8. Expansion device

It reduces the pressure of the refrigerant, and also regulates the flow of the refrigerant to the evaporator. Two widely used types of expansion devices are: capillary tubes and throttle valves (thermostatic expansion valves). Capillary tubes are only used for small units. Once the size and length are fixed, the evaporator pressure, etc. gets fixed. No modifications in operating conditions are possible. Throttle valves are used in larger units. These regulate the flow of the refrigerant according to load on the evaporator.

3.2.9. Evaporator

A common type of evaporator is a coil brazed on to a plate, called a plate evaporator. In a flooded evaporator the coil is filled only with a expansion coil, water or brine may be chilled in the evaporator, and the chilled water or brine may then be used to cool some other medium.
3.3. STANDARD VAPOUR COMPRESSION REFRIGERATION CYCLE

Fig. 3.1 shows the schematic of a standard, saturated, single stage (SSS) vapour compression refrigeration system and the operating cycle on a T-S diagram. As shown in the Fig. the standard single stage, saturated vapour compression refrigeration system consists of the following four processes:

**Process 1-2:** Isentropic compression of saturated vapour in compressor
**Process 2-3:** Isobaric heat rejection in condenser
**Process 3-4:** Isenthalpic expansion of saturated liquid in expansion device
**Process 4-1:** Isobaric heat extraction in the evaporator

In an ideal vapour compression refrigeration cycle, the refrigerant enters the compression at state 1 as saturated vapour and is compressed isentropically to the condenser pressure. The temperature of the refrigerant during this isentropic compression process increases well above the temperature of the surrounding medium.
The refrigerant then enters the condenser as superheated vapour at state 2 and leaves as saturated liquid at state 3 as a result of heat rejection to the surroundings. The temperature of the refrigerant at this state is still above the temperature of the surroundings.

The saturated liquid refrigerant at state 3 is throttled to the evaporator pressure by passing it through an expansion valve or capillary tube. The temperature of the refrigerant drops below the temperature of the refrigerated space during the process. The refrigerant enters the evaporator at state 4 as a low quality saturated mixture, and it evaporates by absorbing heat from the refrigerated space. The refrigerant leaves the evaporator as saturated vapour and re-enters the compressor, completing the cycle.

3.4. ANALYSIS OF VAPOUR COMPRESSION REFRIGERATION CYCLE

A simple analysis of standard vapour compression refrigeration can be carried out by assuming a) steady flow b) negligible kinetic and potential energy changes across each component and c) no heat transfer in connecting pipelines. The steady flow energy equation is applied to each of the four components. The p-h diagram of vapour compression refrigeration was shown in Fig. 3.2.

![P-H diagram of vapour compression refrigeration cycle](image)

Fig.3.2. P-H diagram of vapour compression refrigeration cycle
**Compressor**

The isentropic work input to compressor \((W_{cs}, \text{kJ/s})\) is expressed as:

\[
W_{cs} = m_r (h_2 - h_1)
\]  
(3.1)

where \(h_2\) is the enthalpy of refrigerant at the outlet of compressor (kJ/kg)

The actual compressor work \((W_c, \text{kJ/s})\) is given as

\[
W_{cs} = W_{cs} / \eta_s
\]  
(3.2)

where \(\eta_s\) is the isentropic efficiency.

**Condenser**

The heat rejected by the condenser \((Q_{cond}, \text{kJ/s})\) to the atmosphere is given as

\[
Q_{cond} = m_r (h_2 - h_3)
\]  
(3.3)

where \(h_3\) is the enthalpy of refrigerant at the outlet of condenser (kJ/kg)

**Capillary Tube**

In the capillary tube the enthalpy remains constant (isenthalpy process), therefore,

\[
h_3 = h_4
\]  
(3.4)

Dossat RJ et al. (2002) measured the performance of the refrigeration cycle as coefficient of performance (COP) and is the refrigerating effect produced per unit of work required. It is expressed as:

\[
\text{COP} = Q_{evap} / W_c
\]  
(3.5)

Fatouh M and El Kafafy (2006) defined the volumetric cooling capacity (VCC, kJ/m\(^3\)) as the refrigerating effect per unit volume flow rate at the inlet to the compressor. It is expressed as

\[
Q_{evap} / (m_r / V_s)
\]  
(3.6)

where \(V_s\) is the specific volume at inlet to the compressor (m\(^3\)/kg).
Compressor pressure ratio \( (p_r) \) is given as:

\[
pr = \frac{p_{\text{dis}}}{p_{\text{suc}}} \quad (3.7)
\]

where,

\[
p_{\text{dis}} = \text{refrigerant vapour pressure at the compressor discharge (kN/m}^2\text{)}
\]
\[
p_{\text{suc}} = \text{refrigerant vapour pressure at the compressor suction (kN/m}^2\text{)}.
\]

### 3.5. REFRIGERANT R 134a

R134a is also known as Tetrafluoroethane (CF\(_3\)CH\(_2\)F) from the family of HFC refrigerant. With the discovery of the damaging effect of CFCs and HCFCs refrigerants to the ozone layer, the HFC family of refrigerant has been widely used as their replacement.

It is now being used as a replacement for R-12 CFC refrigerant in the area of centrifugal, rotary screw, scroll and reciprocating compressors. It is safe for normal handling as it is non-toxic, non-flammable and non-corrosive.

Currently it is also being widely used in the air conditioning system in newer automotive vehicles. The manufacturing industry uses it in plastic foam blowing. Pharmaceuticals industry uses it as a propellant.

It exists in gas form when expose to the environment as the boiling temperature is -14.9°F or -26.1°C.

This refrigerant is not 100% compatible with the lubricants and mineral-based refrigerant currently used in R-12. Design changes to the condenser and evaporator need to be done to use this refrigerant. The use of smaller hoses and 30% increase in control pressure regulations also have to be done to the system.
Table 3.1. Properties of Refrigerant R134a

<table>
<thead>
<tr>
<th>No</th>
<th>Properties</th>
<th>R-134a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Boiling Point</td>
<td>-14.9°F or -26.1°C</td>
</tr>
<tr>
<td>2</td>
<td>Auto-Ignition Temperature</td>
<td>1418°F or 770°C</td>
</tr>
<tr>
<td>3</td>
<td>Ozone Depletion Level</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>Solubility In Water</td>
<td>0.11% by weight at 77°F or 25°C</td>
</tr>
<tr>
<td>5</td>
<td>Critical Temperature</td>
<td>252°F or 122°C</td>
</tr>
<tr>
<td>6</td>
<td>Cylinder Color Code</td>
<td>Light Blue</td>
</tr>
<tr>
<td>7</td>
<td>Global Warming Potential (GWP)</td>
<td>1200</td>
</tr>
</tbody>
</table>

3.6. MAIN APPLICATIONS

Tetrafluoroethane (R134a) is a blend component for refrigeration. It also a propellant for aerosol and a blowing agent for extruded polystyrene foams. It replaces the CFC R12 (dichlorodifluoromethane) and in few years the HCFC R22 (chlorodifluoromethane).
3.7. GAS PROPERTIES

- Molecular weight : 102.03 g/mol
- Solid phase
- Melting point (1.013 bar) : -101 °C
- Liquid density (1.013 bar and 25 °C (77 °F)) : 1206 kg/m³
- Boiling point (1.013 bar) : -26.55 °C
- Latent heat of vaporization (1.013 bar at boiling point) : 215.9 kJ/kg
- Vapor pressure (at 20 °C or 68 °F) : 5.7 bar
- Vapor pressure (at 5 °C or 41 °F) : 3.5 bar
- Vapor pressure (at 15 °C or 59 °F) : 4.9 bar
- Vapor pressure (at 50 °C or 122 °F) : 13.2 bar
- Critical temperature : 100.95 °C
- Critical pressure : 40.6 bar
- Critical density : 512 kg/m³
- Triple point temperature : -103.3 °C
- Gas density (1.013 bar at boiling point) : 5.28 kg/m³
- Gas density (1.013 bar and 15 °C (59 °F)) : 4.25 kg/m³
- Compressibility Factor (Z) (1.013 bar and 15 °C (59 °F)) : 1
- Specific gravity : 3.25
- Specific volume (1.013 bar and 15 °C (59 °F)) : 0.235 m³/kg
- Heat capacity at constant pressure (Cp) (1.013 bar and 25 °C (77 °F)) : 0.08754 kJ/(mol.K)
- Solubility in water (1.013 bar and 25 °C (77 °F)) : 0.21 vol/vol
3.8. REFRIGERANT R152a

1,1-Difluoroethane, also DFE is an organofluorine compound with the chemical formula $C_2H_4F_2$. This colorless gas is used as a refrigerant, where it is often listed as R-152a or HFC-152a. As an alternative to chlorofluorocarbons, it has an ozone depletion potential of zero, a lower global warming potential (120) and a shorter atmospheric lifetime (1.4 years). It has recently been approved for use in automobile applications as an alternative to R-134a.

R152a is a colorless gas under ordinary temperature and a colorless and transparent under the pressure of itself, easily soluble in oil but poorly in water. It is mainly used as the important raw material in refrigerant, aerosol propellants and synthesis of R142b. as the substitutive refrigerant for CFC-12, it will be a long term one and have absolutely no bad effects against ozonosphere.

3.9. PROPERTIES AND CHARACTERISTICS OF R 134a AND R152a

Table 3.2. Physical, Safety and Environmental Properties Refrigerant R134a, R152a

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Refrigerant</th>
<th>R134a</th>
<th>R152a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Chemical Formula</td>
<td>$CH_2FCF_3$</td>
<td>$CH_3CHF_2$</td>
</tr>
<tr>
<td>2.</td>
<td>Molecular Mass</td>
<td>102.03</td>
<td>66.05</td>
</tr>
<tr>
<td>3.</td>
<td>Critical Temperature (0 F)</td>
<td>214.00</td>
<td>235.90</td>
</tr>
<tr>
<td>4.</td>
<td>Critical Pressure (psia)</td>
<td>589.00</td>
<td>656.00</td>
</tr>
<tr>
<td>5.</td>
<td>Normal Boiling Point (0 F)</td>
<td>-15.00</td>
<td>-11.20</td>
</tr>
<tr>
<td>6.</td>
<td>Lubricant</td>
<td>POE/PAG</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>Stability</td>
<td>Stable</td>
<td>Stable</td>
</tr>
<tr>
<td>---</td>
<td>----------------------------------------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td>7.</td>
<td>Stability</td>
<td>Stable</td>
<td>Stable</td>
</tr>
<tr>
<td>8.</td>
<td>OSHA Permissible Exposure Limit (ppm)</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>9.</td>
<td>Lower Flammability (% Volume in Air)</td>
<td>None</td>
<td>4.80</td>
</tr>
<tr>
<td>10.</td>
<td>Heat of Combustion (Btu/lbm)</td>
<td>1806</td>
<td>7481</td>
</tr>
<tr>
<td>11.</td>
<td>Safety Group</td>
<td>A1</td>
<td>A2</td>
</tr>
<tr>
<td>12.</td>
<td>Auto Ignition Temperature (0 F)</td>
<td>1418</td>
<td>851</td>
</tr>
<tr>
<td>13.</td>
<td>Atmospheric Life (yr.)</td>
<td>14</td>
<td>2</td>
</tr>
<tr>
<td>14.</td>
<td>Ozone Depletion Potential</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>15.</td>
<td>Global Warming Potential (100 yr.) **</td>
<td>1300</td>
<td>140</td>
</tr>
</tbody>
</table>

POE = Polyolester, PAG = Polyalkylene Glycol, * POE/PAG good candidates for R152a
Safety Group = (A or B) lower and high toxicity respectively, (1, 2, or 3) not flammable, low and high flammability
** GWP for integrated time horizon, and based on 3500 kg CO₂ / kg of R11

### 3.10. SUMMARY

In this chapter review of the relevant study on the vapour compression system, the various components of the vapour compression system and its types were presented. In addition, a detailed study on the refrigerants R134a and R152a along with its properties and applications were discussed. This form the basis for identifying the experimental procedures adopted in the present investigation.
CHAPTER 4
NANOPARTICLES AND SURFACTANTS

4.1. NANO PARTICLES

Nanoparticles and nano particle-based devices are of interest in numerous industrial applications due to their unique and often advantageous properties. The high surface-to-volume ratio together with size effects (quantum effects) of nanoparticles introduces many size-dependent phenomena such as chemical, electronic, magnetic and mechanical properties.

In nanotechnology, a particle is defined as a small object that behaves as a whole unit with respect to its transport and properties. Particles are further classified according to their diameter. Coarse particles cover a range between 10,000 and 2,500 nanometers. Fine particles are sized between 2,500 and 100 nanometers. Ultrafine particles or nano particles are sized between 1 and 100 nanometers. Nanoparticles may or may not exhibit size-related properties that differ significantly from those observed in fine particles or bulk materials. Although the size of most molecules would fit into the above outline, individual molecules are usually not referred to as nanoparticles. Nano powders are agglomerates of ultrafine particles, nanoparticles, or nano clusters. Nanometer-sized single crystals, or single-domain ultrafine particles, are often referred to as nano crystals.

4.1.1. Properties of nano particles

Nanostructure materials are single phase or multiphase polycrystalline solids with a typical average size of a few nanometers (1nm = 10^{-9}m). Basically, the range from 1-100 nm is taken as nano-range for convention as per National Nanotechnology Initiative in the US., and the size of hydrogen atom is considered as the lower limit of nano whereas upper limit is arbitrary. The grain sizes are so small; a significant volume fraction of the atoms resides in grain boundaries. Material is characterized by a large number of interfaces in which the atomic arrangements are different from those of crystal lattice. The basic classification of nonmaterial is done based on the
confinement. Bulk structures show no confinement whereas nano-wells and nano wires can be obtained by 2-D and 1-D confinement respectively. The quantum realm comes to the picture when there is a 3D confinement and leads to zero dimension quantum structures that is quantum dot.

4.2. SYNTHESIS METHODS OF NANO PARTICLES

Synthesis of nano material is most commonly done based on three strategies

- Liquid-phase synthesis
- Gas-phase synthesis
- Vapour-phase synthesis

4.2.1. Liquid-phase synthesis

Under liquid phase synthesis the techniques used for synthesis are:

- Co-precipitation
- Sol-gel Processing
- Micro-emulsions
- Hydrothermal/Solvo-thermal Synthesis
- Microwave Synthesis
- Sono-chemical Synthesis
- Template Synthesis

4.2.2. Gas-phase synthesis

Super saturation is achieved by vapourizing material into a background gas, then cooling the gas.

4.2.3. Methods using solid precursors

- Inert Gas Condensation
- Pulsed Laser Ablation
- Spark Discharge Generation
- Ion Sputtering
4.2.4. Methods using liquid or vapour precursors

- Chemical Vapour Synthesis
- Spray Pyrolysis
- Laser Pyrolysis/ Photochemical Synthesis
- Thermal Plasma Synthesis
- Flame Synthesis
- Flame Spray Pyrolysis
- Low-Temperature Reactive Synthesis

Nanostructured materials can have significantly different properties, depending on the chosen fabrication route. Each method offers some advantages over other techniques while suffering limitation from the others.

In attrition, macro or micro scale particles are ground in a ball mill, a planetary ball mill, or other size reducing mechanism. The resulting particles are air classified to recover nanoparticles. In pyrolysis, a vaporous precursor (liquid or gas) is forced through an orifice at high pressure and burned. The resulting solid (a version of soot) is air classified to recover oxide particles from by-product gases. Pyrolysis often results in aggregates and agglomerates rather than single primary particles.

Thermal plasma can also deliver the energy necessary to cause vaporization of small micrometer size particles. The thermal plasma temperatures are in the order of 10,000 K, so that solid powder easily evaporates. Nanoparticles are formed upon cooling while exiting the plasma region. The main types of the thermal plasma torches used to produce nanoparticles are dc plasma jet, dc arc plasma and Radio Frequency (RF) induction plasmas. In the arc plasma reactors, the energy necessary for evaporation and reaction is provided by an electric arc which is formed between the anode and the cathode. For example, silica sand can be vaporized with arc plasma at atmospheric pressure. The resulting mixture of plasma gas and silica vapour can be rapidly cooled by quenching with oxygen, thus ensuring the quality of the fumed silica produced.
In RF induction plasma torches, energy coupling to the plasma is accomplished through the electromagnetic field generated by the induction coil. The plasma gas does not come in contact with electrodes, thus eliminating possible sources of contamination and allowing the operation of such plasma torches with a wide range of gases including inert, reducing, oxidizing and other corrosive atmospheres. The working frequency is typically between 200 kHz and 40 MHz. Laboratory units run at power levels in the order of 30–50 kW while the large scale industrial units have been tested at power levels up to 1 MW. As the residence time of the injected feed droplets in the plasma is very short it is important that the droplet sizes are small enough in order to obtain complete evaporation. The RF plasma method has been used to synthesize different nanoparticle materials, for example synthesis of various ceramic nanoparticles such as oxides, carbides and nitrides of Ti and Si.

Inert gas condensation is frequently used to make nanoparticles from metals with low melting points. The metal is vaporized in a vacuum chamber and then supercooled with an inert gas stream. The supercooled metal vapor condenses into nanometer-sized particles, which can be entrained in the inert gas stream and deposited on a substrate.

Nanoparticles can also be formed using radiation chemistry. Radiolysis from gamma rays can create strongly active free radicals in solution. This relatively simple technique uses a minimum number of chemicals. These include water, a soluble metallic salt, a radical scavenger (often a secondary alcohol), and a surfactant (organic capping agent). High gamma doses on the order of $10^4$ Gray are required. In this process, reducing radicals will drop metallic ions down to the zero-valence state. A scavenger chemical will preferentially interact with oxidizing radicals to prevent the re-oxidation of the metal. Once in the zero-valence state, metal atoms begin to coalesce into particles. A chemical surfactant surrounds the particle during formation and regulates its growth. In sufficient concentrations, the surfactant molecules stay attached to the particle. This prevents it from dissociating or forming clusters with other particles. Formation of nanoparticles using the radiolysis method allows for
tailoring of particle size and shape by adjusting precursor concentrations and gamma dose.

4.3. ALUMINUM OXIDE (Al₂O₃) NANOPARTICLES

Nanoparticles are being used more and more often in research and in industry, due to their enhanced properties compared to bulk materials. The benefits of nanoparticles can include increased electrical conductivity, toughness and ductility, and increased hardness and strength of metals and alloys.

This article discusses the properties and applications of aluminum oxide nanoparticles. Aluminum is a Block P, Period 3 element, while oxygen is a Block P, Period 2 element.

The morphology of aluminum oxide nanoparticles is spherical, and they appear as a white powder. Aluminum oxide nanoparticles (both liquid and solid forms) are graded as highly flammable and an irritant that can cause serious eye and respiratory irritation.

4.3.1. Chemical properties

The chemical properties of aluminum oxide nanoparticles are outlined in the following table.

<table>
<thead>
<tr>
<th>Chemical Data</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical symbol</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>CAS No.</td>
<td>1344-28-1</td>
</tr>
<tr>
<td>Group</td>
<td>Aluminum 13</td>
</tr>
<tr>
<td></td>
<td>Oxygen 16</td>
</tr>
<tr>
<td>Electronic configuration</td>
<td>Aluminum [Ne]3s²3p³</td>
</tr>
<tr>
<td></td>
<td>Oxygen [He]2s²2p⁴</td>
</tr>
</tbody>
</table>
Table 4.2. Chemical Composition of Al$_2$O$_3$

<table>
<thead>
<tr>
<th>Chemical Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
</tr>
<tr>
<td>Aluminum</td>
</tr>
<tr>
<td>Oxygen</td>
</tr>
</tbody>
</table>

4.3.2. Physical properties

The physical properties of aluminum oxide nanoparticles are given in the following table.

Table 4.3. Physical Properties of Al$_2$O$_3$

<table>
<thead>
<tr>
<th>Properties</th>
<th>Metric</th>
<th>Imperial</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>3.9 g/cm$^3$</td>
<td>0.140 lb/in$^3$</td>
</tr>
<tr>
<td>Molar mass</td>
<td>101.96 g/mol</td>
<td>-</td>
</tr>
</tbody>
</table>

4.3.3. Thermal properties

The thermal properties of aluminum oxide nanoparticles are provided in the table below.

Table 4.4. Thermal Properties of Al$_2$O$_3$

<table>
<thead>
<tr>
<th>Properties</th>
<th>Metric</th>
<th>Imperial</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point</td>
<td>2040°C</td>
<td>3704°F</td>
</tr>
<tr>
<td>Boiling point</td>
<td>2977°C</td>
<td>5391°F</td>
</tr>
</tbody>
</table>
4.3.4. Applications

The key applications of aluminum oxide nanoparticles are listed below:

- In integrate circuit base boards
- Transparent ceramics, high-pressure sodium lamps, and EP-ROM window
- In YAG laser crystals
- As cosmetic fillers
- Single crystal, ruby, sapphire, sapphire, and yttrium aluminum garnets
- High-strength aluminum oxide ceramic and C substrates
- Packaging materials, cutting tools, high purity crucible, winding axle, and furnace tubes
- Polishing materials, glass products, metal products, semiconductor materials
- Plastic, tape, and grinding belts
- Paint, rubber, plastic wear-resistant reinforcement, and advanced waterproof materials
- Catalyst, catalyst carrier, analytical reagents
- Aerospace aircraft wing leading edges
- Vapor deposition materials, special glass, fluorescent materials, composite materials and resins

In cases where aluminum oxide nanoparticles are used in the liquid form such as an aqueous dispersion, the key applications are as follows:

- Plastics, rubber, ceramics, refractory products
- To improve ceramics density, smoothness, fracture toughness, creep resistance, thermal fatigue resistance, and polymer products wear resistance
- Ideal material of far infrared emission
4.4. COPPER OXIDE (CuO) NANOPARTICLES

Nanoparticles research is gaining increasing interest due to their unique properties, such as increased electrical conductivity, toughness and ductility, increased hardness and strength of metals and alloys, luminescent efficiency of semiconductors, formability of ceramics.

This article discusses about the properties and applications of copper oxide nanoparticles. Copper is a Block D, Period 4 element, while oxygen is a Block P, Period 2 element.

Copper oxide nanoparticles appear as a brownish-black powder. They can be reduced to metallic copper when exposed to hydrogen or carbon monoxide under high temperature. They are graded harmful to humans and as dangerous for the environment with adverse effect on aquatic life.

4.4.1. Chemical properties

The chemical properties of copper oxide nanoparticles are outlined in the following table.

Table.4.5. Chemical Properties of CuO

<table>
<thead>
<tr>
<th>Chemical Data</th>
<th>CuO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical symbol</td>
<td>CuO</td>
</tr>
<tr>
<td>CAS No.</td>
<td>1317-38-0</td>
</tr>
<tr>
<td>Group</td>
<td>Copper11</td>
</tr>
<tr>
<td></td>
<td>Oxygen 16</td>
</tr>
<tr>
<td>Electronic configuration</td>
<td>Copper [Ar] 3d^{10} 4s^{1}</td>
</tr>
<tr>
<td></td>
<td>Oxygen [He] 2s^{2} 2p^{4}</td>
</tr>
</tbody>
</table>
Table 4.6. Chemical Composition of CuO

<table>
<thead>
<tr>
<th>Chemical Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
</tr>
<tr>
<td>Copper</td>
</tr>
<tr>
<td>Oxygen</td>
</tr>
</tbody>
</table>

4.4.2. Physical properties

The physical properties of copper oxide nanoparticles are given in the following table.

Table 4.7. Physical Properties of CuO

<table>
<thead>
<tr>
<th>Properties</th>
<th>Metric</th>
<th>Imperial</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>6.31 g/cm³</td>
<td>0.227 lb/in³</td>
</tr>
<tr>
<td>Molar mass</td>
<td>79.55 g/mol</td>
<td></td>
</tr>
</tbody>
</table>

4.4.3. Thermal properties

The thermal properties of copper oxide nanoparticles are provided in the table below.

Table 4.8. Thermal Properties of CuO

<table>
<thead>
<tr>
<th>Properties</th>
<th>Metric</th>
<th>Imperial</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point</td>
<td>1201°C</td>
<td>2194°F</td>
</tr>
<tr>
<td>Boiling point</td>
<td>2000°C</td>
<td>3632°F</td>
</tr>
</tbody>
</table>
4.4.4. Applications

The key applications of copper oxide nanoparticles are as follows:

- It is used as burning rate catalyst in rocket propellant. It can greatly improve the homogeneous propellant burning rate, lower pressure index, and also perform better as a catalyst for the AP composite propellant.
- It is applied to the catalyst, superconducting materials, thermoelectric materials, sensing materials, glass, ceramics and other fields.
- It is used as ceramic resistors, magnetic storage media, gas sensors, near-infrared tilters, photoconductive and photo thermal applications.
- It can be used as semiconductors, solar energy transformation, and high-tech superconductors.

4.5. ZINC OXIDE (ZnO) NANOPARTICLES

Nanotechnology research has gained momentum in the recent years by providing innovative solutions in the field of biomedical, materials science, optics and electronics. Nanoparticles are essentially a varied form of basic elements derived by altering their atomic and molecular properties of elements. This article elaborates on the properties and applications of zinc oxide nanoparticles.

Zinc oxide (ZnO) nanopowders are available as powders and dispersions. These nanoparticles exhibit antibacterial, anti-corrosive, antifungal and UV filtering properties. Zinc is a Block D, Period 4 element while Oxygen is a Block P, Period 2 element. Some of the synonyms of zinc oxide nanoparticles are oxydatum, zinci oxicum, permanent white, ketozinc and oxozinc.
4.5.1. Chemical properties

The chemical properties of zinc oxide nanoparticles are as per the table below.

Table.4.9. Chemical Properties of ZnO

<table>
<thead>
<tr>
<th>Chemical Data</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical symbol</td>
<td>ZnO</td>
</tr>
<tr>
<td>CAS No</td>
<td>1314-13-2</td>
</tr>
<tr>
<td>Group</td>
<td>Zinc 12  Oxygen 16</td>
</tr>
<tr>
<td>Electronic configuration</td>
<td>Zinc [Ar] 3d$^{10}$ 4s$^2$  Oxygen [He] 2s$^2$ 2p$^4$</td>
</tr>
</tbody>
</table>

Table.4.10. Chemical Composition of ZnO

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>Content (%)</td>
</tr>
<tr>
<td>Zinc</td>
<td>80.34</td>
</tr>
<tr>
<td>Oxygen</td>
<td>19.6</td>
</tr>
</tbody>
</table>
4.5.2. Physical properties

The table given below highlights the physical properties of zinc oxide nanoparticles.

Table.4.11. Physical Properties of ZnO

<table>
<thead>
<tr>
<th>Properties</th>
<th>Metric</th>
<th>Imperial</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>5600 kg/m³</td>
<td>0.202 lb/in³</td>
</tr>
<tr>
<td>Molar Mass</td>
<td>81.40 g/mol</td>
<td>-</td>
</tr>
</tbody>
</table>

4.5.3. Thermal properties

Given below are the thermal properties of zinc oxide nanoparticles.

Table.4.12. Chemical Properties of ZnO

<table>
<thead>
<tr>
<th>Properties</th>
<th>Metric</th>
<th>Imperial</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point</td>
<td>1975°C</td>
<td>3587°F</td>
</tr>
<tr>
<td>Boiling point</td>
<td>2360°C</td>
<td>4280°F</td>
</tr>
</tbody>
</table>

4.5.4. Applications

Some of the applications of zinc oxide nanoparticles are given below.

- Zinc oxide is used in the manufacture of rubber and cigarettes (used as a filter).
- Popularly known calamine lotion is made out of zinc oxide powder. It is also used in a host of other creams and ointments that are used to treat skin diseases.
- As an additive in the manufacture of concrete.
- Ceramic industry has a number of uses for zinc oxide powder.
• It is also used as an additive in food products such as breakfast cereals.
• Various paints use zinc oxide as a coating agent.

4.6. CHARACTERIZATION

Nano particle characterization is necessary to establish understanding and control of nano particle synthesis and applications. Characterization is done by using a variety of different techniques, mainly drawn from materials science. The common techniques are:

• Electron microscopy (TEM, SEM)
• Atomic force microscopy (AFM)
• Dynamic light scattering (DLS)
• X-ray photoelectron spectroscopy (XPS)
• Powder X-ray diffraction (XRD)
• Fourier transforms infrared spectroscopy (FTIR)
• Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF)
• Ultraviolet-visible spectroscopy
• Dual polarization interferometer
• Nuclear magnetic resonance (NMR)

4.7. SURFACTANTS

Surfactant, also called surface-active agent, substance such as a detergent that, when added to a liquid, reduces its surface tension, thereby increasing its spreading and wetting properties. In the dyeing of textiles, surfactants help the dye penetrate the fabric evenly. They are used to disperse aqueous suspensions of insoluble dyes and perfumes. The surface-active molecule must be partly hydrophilic (water-soluble) and partly lipophilic (soluble in lipids, or oils). It concentrates at the interfaces between bodies or droplets of water and those of oil, or lipids, to act as an emulsifying agent, or foaming agent. Other surfactants that are more lipophilic and less hydrophilic may be used as defoaming agents, or as demulsifiers. Certain surfactants are
germicides, fungicides, and insecticides. Surfactants are used in corrosion inhibition, in ore flotation, to promote oil flow in porous rocks, and to produce aerosols.

4.7.1. Properties

Surfactants reduce the surface tension of water by adsorbing at the liquid-gas interface. They also reduce the interfacial tension between oil and water by adsorbing at the liquid-liquid interface. Many surfactants can also assemble in the bulk solution into aggregates. Examples of such aggregates are vesicles and micelles. The concentration at which surfactants begin to form micelle is known as the critical micelle concentration (CMC). When micelles form in water, their tails form a core that can encapsulate an oil droplet, and their (ionic/polar) heads form an outer shell that maintains favorable contact with water. When surfactants assemble in oil, the aggregate is referred to as a reverse micelle. In a reverse micelle, the heads are in the core and the tails maintain favorable contact with oil. Surfactants are also often classified into four primary groups; anionic, cationic, non-ionic, and zwitterionic (dual charge).

4.7.2. Amphiphiles

The word amphiphile was coined by Paul Winsor 50 years ago. It comes from two Greek roots. First the prefix *amphi* which means "double", "from both sides", "around", as in amphitheater or amphibian. Then the root *philos* which expresses friendship or affinity, as in "philanthropist" (the friend of man), "hydrophilic" (compatible with water), or "philosopher" (the friend of wisdom or science).

An amphiphilic substance exhibits a double affinity, which can be defined from the physico-chemical point of view as a polar-apolar duality. A typical amphiphilic molecule consists of two parts: on the one hand a polar group which contains heteroatoms such as O, S, P, or N, included in functional groups such as alcohol, thiol, ether, ester, acid, sulfate, sulfonate, phosphate, amine, amide etc… On the other hand, an essentially apolar group which is in general an hydrocarbon chain of the alkyl or alkylbenzene type, sometimes with halogen atoms and even a few nonionized oxygen atoms.
The polar portion exhibits an strong affinity for polar solvents, particularly water, and it is often called hydrophilic part or hydrophile. The apolar part is called hydrophobe or lipophile, from Greek roots *phobos* (fear) and *lipos* (grease). The following formula shows an amphiphilic molecule which is commonly used in shapoos (sodium dodecyl sulfate).

4.7.3. Tension lowering agent versus surfactant

Because of its dual affinity, an amphiphilic molecule does not feel "at ease" in any solvent, be it polar or non polar, since there is always one of the groups which "does not like" the solvent environment. This is why amphiphilic molecules exhibit a very strong tendency to migrate to interfaces or surfaces and to orientate so that the polar group lies in water and the apolar group is placed out of it, and eventually in oil.

In the following the word surface will be used to designate the limit between a condensed phase and a gas phase, whereas the term interface will be used for the boundary between two condensed phases. This distinction is handy though not necessary, and the two words are often used indifferently particularly in American terminology.

In English the term surfactant (short for surface-active-agent) designates a substance which exhibits some superficial or interfacial activity. It is worth remarking that all amphiphiles do not display such activity; in effect, only the amphiphiles with more or less equilibrated hydrophilic and lipophilic tendencies are likely to migrate to the surface or interface. It does not happen if the amphiphilic molecule is too hydrophilic or too hydrophobic, in which case it stays in one of the phases.

Amphiphiles exhibit other properties than tension lowering and this is why they are often labeled according to their main use such as: soap, detergent, wetting agent, disperssant, emulsifier, foaming agent, bactericide, corrosion inhibitor, antistatic agent, etc… In some cases they are konwn from the name of the structure they are able to build, i.e. membrane, microemulsion, liquid crystal, liposome, vesicle or gel.
4.7.4. Classification of surfactants

Surfactants are generally classified as

i) Ionic
   a) Anionic
      • Sodium dodecyl sulfate (SDS)
      • Sodium laureth sulfate (SLS)
   b) Cationic
      • Cetyl trimethyl ammonium bromide (CTAB)
      • Cetyl pyridinium chloride (CPC)
   c) Zwitterionic
      • Dodecyl betaine
      • Cocamido propyl betaine

ii) Non Ionic
    • Alkyl poly ethylene oxide
    • Cetyl alcohol

4.7.5. Anionic surfactants

Anionic surfactants contain anionic functional groups at their head, such as sulfate, sulfonate, phosphate, and carboxylates. Prominent alkyl sulfates include ammonium lauryl sulfate, sodium lauryl sulfate (SDS, sodium dodecyl sulfate, another name for the compound) and the related alkyl-ether sulfates sodium laureth sulfate, also known as sodium lauryl ether sulfate (SLES), and sodium myreth sulfate.
4.7.6. Sodium dodecyl sulphate (SDS)

Sodium dodecyl sulfate (SDS or NaDS), sodium laurilsulfate or sodium lauryl sulfate (SLS) is an organic compound with the formula CH$_3$(CH$_2$)$_{11}$OSO$_3$Na. It is an anionic surfactant used in many cleaning and hygiene products. The salt is of an organosulfate consisting of a 12-carbon tail attached to a sulfate group, giving the material the amphiphilic properties required of a detergent. Derived from inexpensive coconut and palm oils, it is a common component of many domestic cleaning products.

4.7.7. Application and properties of SDS

SDS is mainly used in detergents for laundry with many cleaning applications. SDS is a highly effective surfactant and is used in any task requiring the removal of oily stains and residues. For example, it is found in higher concentrations with industrial products including engine degreasers, floor cleaners, and car wash soaps. CMC of SDS varies with pH.

Table 4.13. Properties of Sodium Dodecyl Sulphate (SDS)

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>NaC$<em>{12}$H$</em>{25}$SO$_4$</td>
</tr>
<tr>
<td>Molar mass</td>
<td>288.372 g/mol</td>
</tr>
<tr>
<td>Appearance</td>
<td>white or cream-colored solid</td>
</tr>
<tr>
<td>Odor</td>
<td>odorless</td>
</tr>
<tr>
<td>Density</td>
<td>1.01 g/cm$^3$</td>
</tr>
<tr>
<td>Melting point</td>
<td>206 °C (403 °F; 479 K)</td>
</tr>
<tr>
<td>Refractive index ($n_D$)</td>
<td>1.461</td>
</tr>
</tbody>
</table>
4.8. CATIONIC SURFACTANTS

Cationic Surfactants are dissociated in water into an amphiphilic cation and an anion, most often of the halogen type. A very large proportion of this class corresponds to nitrogen compounds such as fatty amine salts and quaternary ammoniums, with one or several long chain of the alkyl type, often coming from natural fatty acids. These surfactants are in general more expensive than anionics, because of the high pressure hydrogenation reaction to be carried out during their synthesis. As a consequence, they are only used in two cases in which there is no cheaper substitute, i.e. (1) as bactericide, (2) as positively charged substance which is able to adsorb on negatively charged substrates to produce antistatic and hydrophobant effect, often of great commercial importance such as in corrosion inhibition.

4.8.1. Cetrimonium bromide (CTAB)

Cetrimonium bromide (\((\text{C}_{16}\text{H}_{33})\text{N(CH}_3\text{)}_3\text{Br, cetyltrimethylammonium bromide, hexadecyltrimethylammonium bromide, CTAB}\)) is one of the components of the topical antiseptic cetrimide. The cetrimonium (or hexadecyltrimethylammonium) cation is an effective antiseptic agent against bacteria and fungi.

It is a cationic surfactant. Its uses include providing a buffer solution for the extraction of DNA. It has been widely used in synthesis of gold nanoparticles (e.g., spheres, rods, bipyramids) and mesoporous silica nanoparticles (e.g., MCM-41). It is also widely used in hair conditioning products.

As any surfactant, it forms micelles in aqueous solutions. At 303 K (30 °C) it forms micelles with aggregation number 75-120 (depending on method of determination, usually average ~95) and degree of ionization \(\alpha\) (fractional charge) 0.2–0.1 (from low to high concentration).

The standard constant of Br- counterion binding to the micelle at 303 K (30 °C) is \(K^° \approx 400\). This value is calculated from Br- and CTA+ ion selective electrode measurements and conductometry data by using literature data for micelle size \((r = \sim 3 \text{ nm})\), extrapolated to the critical micelle concentration of 1 mM. However, it
varies with total surfactant concentration so it is extrapolated to the point at which the concentration of micelles is zero.

The closely related compounds cetrimonium chloride and cetrimonium stearate are also used as topical antisepsics, and may be found in many household products such as shampoos and cosmetics, while cetrimonium bromide, due to its high cost, is only found in select cosmetics.

4.8.2. Properties of CTAB

<table>
<thead>
<tr>
<th>Properties</th>
<th>Cetrimonium bromide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C₁₀H₂₂BrN</td>
</tr>
<tr>
<td>Molar mass</td>
<td>364.45 g/mol</td>
</tr>
<tr>
<td>Appearance</td>
<td>white powder</td>
</tr>
<tr>
<td>Melting point</td>
<td>237–243 °C (decomposes)</td>
</tr>
</tbody>
</table>

4.9. ZWITTERIONIC SURFACTANTS

Zwitterionic (amphoteric) surfactants have both cationic and anionic centers attached to the same molecule. The cationic part is based on primary, secondary, or tertiary amines or quaternary ammonium cations. The anionic part can be more variable and include sulfonates.

When a single surfactant molecule exhibit both anionic and cationic dissociations it is called amphoteric or zwitterionic. This is the case of synthetic products like betaines or sulfobetaines and natural substances such as aminoacids and phospholipids.
4.10. SUMMARY

A detailed study and analysis and nano particles, their properties, synthesis and techniques were presented in this chapter. Understanding of physical, chemical and thermal properties enables to choose the suitable nano particles for the present work. In addition to this a detailed investigation on surfactants and its types with their properties was also present in this chapter.
CHAPTER 5

EXPERIMENTAL SETUP AND PREPARATION OF THE NANOFLUIDS

5.1. FABRICATION OF EXPERIMENTAL SETUP

The experimental consists of a compressor, fan cooled condenser, expansion device and an evaporator section. Capillary tube is used as an expansion device. The evaporator is of serpentine coil type which is loaded with water. Service ports are provided at the inlet of expansion device and compressor for charging the refrigerant. The mass flow rate is measured with the help of flow meter fitted in the line between expansion device and drier unit. The experimental setup was placed on a platform in a constant room temperature. The ambient temperature was ±1.5°C. The air flow velocity was found to be less than 0.25m/s.

![Fig.5.1. Photograph of the experimental setup](image-url)
5.2. MEASUREMENT OF PARAMETERS

The temperatures at different parts of the experimental setup are measured using resistance thermocouples. 8 numbers of resistance thermocouples were used for the experimentation. The pressure at compressor suction, discharge, condenser outlet and at evaporator outlet are measured with the help of pressure gauges. The power consumption of the system was measures by a digital Watt-hr meter. A digital wattmeter and flow meter were also connected with the experimental setup. Table.5.1. summarized the characteristics of the instrumentation.

Table.5.1. Measurement equipments

<table>
<thead>
<tr>
<th>Variable</th>
<th>Device</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>Pt100 PID controller</td>
<td>-50 to 199°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>Pressure Gauge</td>
<td>0-10 bar</td>
</tr>
<tr>
<td>Power</td>
<td>Digital Watt/Watt-h meter</td>
<td>5-20A</td>
</tr>
</tbody>
</table>

Fig.5.2. Schematic representation of the experimental setup
5.3. MOUNTING OF THERMOCOUPLES

Refrigeration test rig was developed in order to investigate the performance of the system. In developing the reliable refrigerator test rig, consideration should be highly addressed especially the development method and measurement locations of pressure and temperature. These are very important to ensure that the test rig can produce reliable data. Pannock, J et al. (1994), Philipp, J et al. (1996), Mc Keller and Tree, D.R (1988) and Melo, C and Pereira, R. H (1988) discussed the development of refrigerator test rig. They discussed the locations of temperature and pressure measurement points, measurement devices and measurement methods. There are eight points of temperature measurement, four points of pressure measurement and one point of flow rate measurement.

From the eight points of temperature measurement, six points have been placed in the refrigeration circuit to measure refrigerant temperature and another two points have been placed in the evaporator compartment. The same number of points and locations were adopted by Pannock, J et al. (1994), Philipp, J et al. (1996), Mc keller and Tree, D.R (1988) and Melo, C and Pereira, R. H (1988) who followed several standards such as ANSI/AHAM HRF-1988 (AHAM 1988) and European standard for measuring the energy consumption of electric mains operated on household refrigerators (DIN EN 153). The thermocouple wire was used to measure the temperature of refrigerant in the tube (ANSI/ASHRAE Standard, 1986). The technique to measure the temperature is the same as Philipp et al (1996), where the thermocouple wire was put inside the refrigerant tube so that the measurement made was exactly the temperature of the refrigerant. However, the method to construct the sensor was different. Fig 3 shows the method to construct the temperature measurement point in the refrigerant tube.

By using this method, A suitable length of copper tube with flared end was used to hold a thermocouple wire which was inserted into the tube and effectively sealed. The flared tube is fitted securely on to a copper T-junction which was then joined mechanically to the tube to reconnect every two consecutive components. The temperature of the refrigerant which now flowed through each T-junction was measured
by the hot thermocouple junction or head. Prior to installation each thermocouple was calibrated using a platinum thermocouple against temperature of freezing point, room condition and boiling point of water. Table 1 shows the three sets of data with different conditions of water used during calibration. The thermocouple used was of T-type, 0.3 mm diameter and designed for temperature range between -50°C to 250°C. The accuracy is about ±2%.

Fig 5.3. Construction method of temperature measurement point
Table 5.2: Calibration data of thermocouple points

<table>
<thead>
<tr>
<th>Thermocouple Type / No.</th>
<th>Temperature Measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Freezing</td>
</tr>
<tr>
<td>Platinum No. 1</td>
<td>0°C</td>
</tr>
<tr>
<td>No. 2</td>
<td>-0.3°C</td>
</tr>
<tr>
<td>No. 3</td>
<td>-0.2°C</td>
</tr>
<tr>
<td>No. 4</td>
<td>-0.2°C</td>
</tr>
<tr>
<td>No. 5</td>
<td>-0.2°C</td>
</tr>
<tr>
<td>No. 6</td>
<td>0°C</td>
</tr>
<tr>
<td>No. 7</td>
<td>-0.1°C</td>
</tr>
<tr>
<td>No. 8</td>
<td>-0.1°C</td>
</tr>
</tbody>
</table>

Besides that, four points of pressure were tapped respectively made on pipes connecting all main components. Experimental works of Pannock, J et al. (1994), Philipp, J et al. (1996), and Melo, C and Pereira, R. H (1988) only measured suction and discharge pressures of compressor while the present works allowed pressure drops across each component and along connecting pipes to be known (Jones, 2001, ASHRAE, 2001). Bourdon Tube pressure gauges were used for each pressure measurement in this test rig (ANSI/ASHRAE Standard, 1989, ARI 1998). A tube with diameter 2.1 mm was used to connect the refrigerant tube to each pressure gauge as what was done by Philipp. Fig 4 shows the detail construction of the pressure measurement points.
In this work a metal tube flow meter indicator was used. This flow meter was manufactured and calibrated by Brooks Instruments. The flow meter was assembled between condenser and capillary tube to measure the refrigerant flow rate in liquid form in g/s. A sight glass was installed before the flow meter to observe the liquid phase of the refrigerant. When there were no bubbles observed the flow was taken as that of a fully liquid refrigerant (Eugene, 2002, Jones, 2001).

5.4. LEAK PROOF TESTING AND CHARGING OF EXPERIMENTAL SETUP

The fabricated experimental setup was filled with N₂ gas at a pressure of 5 to 7 bar and this pressure is maintained for 5 hrs. Thus the system was ensured for no leakages. The system was evacuated by removing N₂ gas. A vacuum pump was connected to the port provided in the compressor and the system was completely
evacuated for the removal of any impurities. This process was carried out for all the trials. The refrigerant R152a was charged through the charging line to the compressor. Precision electronic balance with accuracy ±1% was used to charge into the system. Every time the system was allowed to stabilize for 10 min.

5.5. PREPARATION AND CHARACTERIZATION OF NANO FLUIDS

5.5.1 Equipments used for characterization of nano fluids

The equipments which were used for characterization of nano fluids are SEM, EDXS, XRD and KD2 Pro thermal analyzer.

5.5.2. Scanning electron microscope (SEM)

A scanning electron microscope (SEM) as shown in Fig 5.5 is a type of electron microscope that produces the images of a sample by scanning it with a focused beam of electrons. The electrons interact with electrons in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image. SEM can achieve resolution better than 1 nanometer. Specimens can be observed in high vacuum, low vacuum and environmental SEM specimens can be observed in wet conditions.

The types of signals produced by a SEM include secondary electrons (SE), back-scattered electrons (BSE), characteristic X-rays, light (cathode luminescence) (CL), specimen current and transmitted electrons. The SEM can produce very high-resolution images of a sample surface, revealing details less than 1 nm in size. A wide range of magnifications is possible, from about 10 times (about equivalent to that of a powerful hand-lens) to more than 500,000 times, about 250 times the magnification limit of the best light microscopes.
In a typical SEM, an electron beam is thermionically emitted from an electron gun fitted with a tungsten filament cathode. Tungsten is normally used in thermionic electron guns because it has the highest melting point and lowest vapour pressure of all metals, thereby allowing it to be heated for electron emission, and because of its low cost. Other types of electron emitters include lanthanum hexaboride (LaB₆) cathodes, which can be used in a standard tungsten filament SEM if the vacuum system is upgraded and FEG, which may be of the cold-cathode type using tungsten single crystal emitters or the thermally assisted Schottky type, using emitters of zirconium oxide.

The electron beam, which typically has an energy ranging from 0.2 keV to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the x and y axes so that it scans in a faster fashion over a rectangular area of the sample surface.

When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a tear drop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 µm into the surface. The SEM used in this study is of Make: Hitachi, Model: S-3400N, resolution: 3nm@30kV and magnification: 5X to 300,000X.
5.6. ENERGY-DISPERSIVE X-RAY SPECTROSCOPY (EDXS)

Energy-dispersive X-ray spectroscopy (EDXS) is an analytical technique which is used for the elemental analysis or chemical characterization of a sample. It relies on the investigation of an interaction of some source of X-ray excitation and a sample. The intensity or area of a peak in an EDX spectrum is proportional to the concentration of the corresponding element in the specimen. For determining elemental content, the electron-beam current is assumed to be uniform throughout the specimen and electron channeling is avoided by avoiding strong diffraction conditions. Energy Dispersive X-ray Analysis (EDXA) technique is used for performing chemical analysis in conjunction with Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). It is not a surface science technique. The analytical data is acquired in the form of digitized spectra, viewed during accumulation on a computer monitor, which displays the number of X-rays, \( I \), detected as a function of \( E \), the X-ray energy.

An electron beam strikes the surface of conducting sample (SEM). The energy of the beam is typically in the range of 10-20 keV. This causes X-rays to be emitted from the irradiated material. The energy of the X-rays emitted depends on the material under examination. The X-rays are generated in a region about 2 microns in depth (SEM), and thus EDX is not a surface science technique. By moving the electron beam across the material and 2-D (two dimensional) image of each element in the sample can be acquired. Due to the low X-ray intensity, images usually take a number of hours to be acquired. Elements of low atomic number are difficult to detect by EDX. A Beryllium window is often used to protect the SiLi detector in the EDX system. The absorption of the soft X-rays precludes the detection of elements below an atomic number of 11 (Na). In windowless EDX systems, elements with as low atomic number as 4 (Be) have been detected, but the problems involved get progressively worse as the atomic number is reduced.
5.6.1. X-Ray diffractometer

An X-ray diffractometer illuminates a sample of material with X-rays of known wavelength, moving the sample and detector in order to measure the intensity of the diffracted radiation as a function of beam and sample orientation. From the resulting intensity versus angle plot much can be inferred about the structure of the material. A diffractometer can be used to make a diffraction pattern of any crystalline solid. With a diffraction pattern an investigator can identify an unknown mineral, or characterize the atomic-scale structure of an already identified mineral.

Diffraction occurs as waves interact with a regular structure whose repeat distance is about the same as the wavelength. The phenomenon is common in the natural world, and occurs across a broad range of scales. For example, light can be diffracted by a grating having scribed lines spaced on the order of a few thousand angstroms, about the wavelength of light. It happens that X-rays have wavelengths on the order of a few angstroms, the same as typical interatomic distances in crystalline solids. That means X-rays can be diffracted from minerals which, by definition, are crystalline and have regularly repeating atomic structures.

5.6.2. X-RAY DIFFRACTION TECHNIQUE

Fig.5.6. X-ray Diffraction principle in accordance with Bragg’s Law
Until 1895 the study of matter at the atomic level was a difficult task but the discovery of electromagnetic radiation with 1 Å (10-10 m) wavelength, appearing at the region between gamma-rays and ultraviolet, makes it possible. As the atomic distance in matter is comparable with the wavelength of X-ray, the phenomenon of diffraction find its way through it and gives many promising results related to the crystalline structure. The unit cell and lattices which are distributed in a regular three-dimensional way in space forms the base for diffraction pattern to occur. These lattices form a series of parallel planes with its own specific d-spacing and with different orientations exist. The reflection of incident monochromatic X-ray from successive planes of crystal lattices when the difference between the planes is of complete number n of wavelengths leads to famous Bragg’s law:

\[ n \lambda = 2d \sin \theta \]

Where n is an integer 1, 2, 3….. (Usually equal 1), \( \lambda \) is wavelength in angstroms (1.54 Å for copper), d is inter atomic spacing in angstroms, and \( \theta \) is the diffraction angle in degrees. Plotting the angular positions and intensities of the resultant diffracted peaks of radiation produces a pattern, which is characteristic of the sample. The fingerprint characterization of crystalline materials and the determination of their structure are the two fields where XRD has been mostly used. Unique characteristic X-ray diffraction pattern of each crystalline solid gives the designation of “fingerprint technique” to XRD for its identification. XRD may be used to determine its structure, i.e. how the atoms pack together in the crystalline state and what the interatomic distance and angle are etc. From these points it can be concluded that X-ray diffraction has become a very important and powerful tool for the structural characterization in solid state physics and materials science.
The crystal size of the particle is calculated using the Debye-Scherrer formula as shown in equation 5.1.

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]  \hspace{1cm} \text{Eq. 5.1}

Where D is the size of the particle, \( \lambda \) is the X-ray wavelength (1.5406), \( \beta \) is the peak width and theta is the Braggs angle.

5.7. KD2 Pro thermal analyser

The KD2 Pro is a battery-operated, menu-driven device. It consists of a handheld microcontroller and sensor needles. The KD2’s sensor needle contains both a heating element and a thermistor. The controller module contains a battery, a 16-bit microcontroller/AD converter, and power control circuit. The thermal conductivity measurement assumes: (i) the long heat source can be treated as an infinitely long heat source (ii) the medium is both homogeneous and isotropic, and at uniform initial temperature, \( T_0 \). The sensor needle used is KS-1 which is made of stainless steel having a length of 60 mm and a diameter of 1.3 mm, and closely approximates the infinite line heat source which gives least disturbance to the sample during measurements. The sensor
needle can be used for measuring thermal conductivity of fluids in the range of 0.2–2 W/mK with an accuracy of ±5%.

![KD2 Pro thermal analyzer](image)

**Fig 5.8. KD2 Pro thermal analyzer**

Each measurement cycle consists of 90s. During the first 30 s, the instrument will equilibrate which is then followed by heating and cooling of sensor needle for 30 s each. At the end of the cycle, the controller computes the thermal conductivity using the change in temperature (ΔT) – time data from equation 5.2.

\[
K = \frac{q(\ln t_2 - \ln t_1)}{4\pi(\Delta T_2 - \Delta T_1)} \tag{Eq. 5.2}
\]

Where q is constant heat rate applied to an infinitely long and small line source, ΔT₁ and ΔT₂ are the changes in the temperature at times t₁ and t₂ respectively.

The KD2 analyzer used in our experiments collects data at 1 s intervals during a 30 s heating time and a 30 s cooling time. The final 20 points during heating and cooling are used in a simultaneous least squares computation which determines the thermal conductivity. Temperature is measured by a 16 bit analog to digital converter. All of the computations are done by an internal 16 bit microcontroller, and the result is displayed. The calibration of the sensor needle is carried out first by measuring thermal conductivity of distilled water and glycerine. The measured values for distilled water and glycerin are
0.611 and 0.292 W/mK respectively which are in agreement with the literature values of 0.613 and 0.285 W/mK respectively within ±5% accuracy (Hagen 1999, Vargaftik 1975, Kothandaraman 2007). The calibration of the KD2 Pro sensor needle is carried out at room temperature (32°C) and the uncertainty in measurements is calculated as ±2% on the basis of 95% confidence level.

5.8. SYNTHESIS OF NANOFLUID

Preparation of nano fluids is the first key step in experimental studies with nano fluids. Nano fluids are not just dispersion of solid particles in a fluid. The essential requirements that a nano fluid must fulfill are even and stable suspension, adequate durability, negligible agglomeration of particles, no chemical change of the particles or fluid, etc. Nanofluids are produced by dispersing nanometer scale solid particles into base liquids such as water, ethylene glycol, oil, etc. In the synthesis of nano fluids, agglomeration is a major problem.

5.8.1. Two step method synthesis of nanofluids

The two-step method is extensively used in the synthesis of nano fluids considering the available commercial nano-powders supplied by several companies. In this method, nanoparticles were first produced and then dispersed in the base fluids. Generally, ultrasonic equipment is used to intensively disperse the particles and reduce the agglomeration of particles. As compared to the single-step method, the two-step technique works well for oxide nanoparticles, while it is less successful with metallic particles. Except for the use of ultrasonic equipment, some other techniques such as control of pH or addition of surface active agents are also used to attain stability of the suspension of the nano fluids against sedimentation. These methods change the surface properties of the suspended particles and thus suppress the tendency to form particle clusters. In this work two step method was incorporated for the preparation of the nano-fluids (nano lubricants).
5.8.2. Critical issues involved in and after nano fluid synthesis

The inherent difficulties associated with characterizing the particle size and dispersion characteristics of nano fluids further complicate the study of heat transport in these suspensions. The nanometer-scale of the particle additions dramatically limits the options available for sample characterization. Electron microscopy techniques are by far the most commonly available methods to image nano-size objects. Traditional electron microscopes, however, require a nano fluid sample to be dried before it can be imaged in a vacuum. Therefore, additional agglomeration resulting from the drying process (as well as clumping structures that might be destroyed in the process) would tend to render the results as non-representative. In addition, the resulting images also represent a very small snapshot of the fluid, and therefore, many carefully chosen samples are required to ensure data is representative of the entire sample. Alternative methods include “wet-cell” electron microscopy where images are taken of samples that remain in solution, small angle x-ray diffraction scattering (SAXS), and dynamic light scattering (DLS). The latter two options are particularly attractive because they can provide full particle size distribution data that is representative of the entire sample. Although, for SAXS some concerns include an upper cut off on detectable size and possible interaction effects.

During sonication, bubbles are created and collapsed, and the resulting shock from this cavitation process breaks up nano particles agglomerates. However, the process also generates heat and the nano fluid temperature rises, especially in continuous mode sonication. In order to mitigate evaporation of the base fluid during sonication, a cooling system should be employed during the continuous mode sonication.

The lack of nano particle dispersion within nano fluids appears to be a limiting factor in the effectiveness of their heat transfer. Agglomeration issues must be overcome in order to obtain the full potential of nano fluid heat transfer. Agglomeration and size characterization issues are current limitations to the usefulness and understanding of nano fluids.
The preparation of the nano fluid in our project involved three phases. They are as follows.

5.9. HOMOGENISING OF NANO PARTICLES IN THE LUBRICANT

Three lubricants bottles of Sanden SP-10 lubricant was taken 250 ml in each beaker. The nano particles CuO of 0.05%v was taken and added to one of the beaker containing the lubricant. The same procedure was followed for the rest of the two ZnO and Al₂O₃ samples. It is manually stirred first and then closed tightly with a cap and shaken properly to get it mixed well.

![Fig.5.9. Mixing of Nano particles of Al₂O₃, ZnO and CuO](image)

5.9.1. Magnetic stirring

A magnetic stirrer or magnetic mixer is a laboratory device that employs a rotating magnetic field to cause a stir bar immersed in a liquid to spin very quickly, thus stirring it. The rotating field may be created either by a rotating magnet or a set of stationary electromagnets, placed beneath the vessel with the liquid. A stir bar is the magnetic bar placed within the liquid which provides the stirring action. The stir bar's motion is driven by another rotating magnet or assembly of electromagnets in the stirrer device, beneath the vessel containing the liquid.
Fig. 5.10. Magnetic stirring process of Al$_2$O$_3$, ZnO and CuO nano particles

They are bar shaped and often octagonal in cross-section (sometimes circular), although a variety of special shapes exist for more efficient stirring. Most stir bars have a ridge around the center (called a pivot ring) on which they rotate. Magnetic stirring was done for 6 hours for each sample of the nano fluid sample that was prepared earlier.

5.9.2. Ultrasonication

Ultrasonication process is done by an ultrasonic bath. An ultrasonic bath is a high frequency electrical energy that is converted into ultrasound waves by means of ultrasonic transducers, which are bonded on the base of S.S. water tank. The ultrasonic bath sonicator are high frequency sound waves that are created in the liquid countless, microscopic vacuum bubbles, which rapidly expand & collapse. This phenomenon is cavitation. The bubbles act like miniature high speed brushes, driving the liquid into all openings and minutes recesses of the object immersed in the liquid.

Fig. 5.11. Ultrasonication process of Al$_2$O$_3$, ZnO and CuO Nano particles
Ultrasonic baths can be used for cleaning or indirect contact homogenization. The high frequency sound waves provide the necessary action for the homogenization and the uniform agglomeration of the nano particles in the lubricant.

![Synthesized Nano lubricants of Al2O3, ZnO and CuO with no particle settlement](image)

**Fig.5.12.** Synthesized Nano lubricants of Al2O3, ZnO and CuO with no particle settlement

Nano fluid samples thus prepared are kept for observation and no particle settlement was observed at the bottom of the flask containing nano fluids even after 24 hours. Thus Nano lubricants with Alumina, Zinc oxide, Copper oxide were synthesized by Magnetic stirring and Ultrasonication process

**5.10. CHARACTERIZATION OF COPPER OXIDE NANOFUID**

The characterization of copper oxide nanoparticles were done by XRD for structural determination and estimation of crystalline size using the instrument PANalytical X’Pert PRO diffractometer and the average size of the nanoparticle were calculated using Debye-Scherrer equation 5.1 and it was 50 nm and image for XRD is shown in Fig 5.13

Scanning Electron Microscope and Energy Dispersive X-ray Analysis (EDXA) is done using the instrument Hitachi, model: S-3400 N for surface morphology and chemical analysis. The result showed that the copper oxide nanoparticle is spherical in shape and the presence Cu and O elements are confirmed Fig 5.16 shows the image of...
dispersed copper oxide nanoparticle in base fluid and the thermal conductivity is measured using KD2 Pro thermal analyzer, Decagon Devices, Inc., USA. The value is found to be 0.698 W/mK and showed an increase of 12.4 % when compared to DI Water (0.613 W/mK).

**Fig 5.13.** X-ray diffractogram for the copper oxide nanoparticles

**Fig 5.14.** SEM Micrograph (5000X) of CuO nanoparticles

**Fig 5.14.** SEM Micrograph (5000X) of CuO nanoparticles
Fig. 5.15. EDX diffractogram of CuO nanoparticles

Fig. 5.16. SEM image for copper oxide nanofluid
5.11. CHARACTERIZATION OF ALUMINIUM OXIDE NANOFUID

The characterization of Aluminium oxide nanoparticles were done by XRD, SEM, EDXA and KD2 Pro thermal analyzer. Using the instrument PAnalytical X’Pert PRO diffractometer the structural determination and estimation of crystalline size were carried out. The average size of the nanoparticle was calculated using Debye-Scherrer equation 5.1 and it was 50 nm. The image for XRD is shown in Fig 5.17.

Scanning electron microscope and energy dispersive X-ray analysis (EDXA) is done using the instrument Hitachi, model: S-3400 N for surface morphology and chemical analysis. The result showed that the aluminum oxide nanoparticle is spherical in shape is shown in Fig 5.19 and the presence of Al and O elements are confirmed. Fig 5.20 shows the image of dispersed aluminum oxide nanoparticle in base fluid and the thermal conductivity is measured using KD2 Pro thermal analyzer, Decagon Devices, Inc., USA. The value is found to be 0.6507W/mK which showed an increase of 5.8 % when compared to DI Water (0.613 W/mK).

![X- Ray diffraction pattern of Al₂O₃](image)

Fig.5.17. X- Ray diffraction pattern of Al₂O₃
Fig. 5.18. SEM Micrograph (5000X) of Al$_2$O$_3$ Nanoparticles

Fig. 5.19. EDX diffractogram of Al$_2$O$_3$ nanoparticles
5.12. CHARACTERIZATION OF ZINC OXIDE NANOFLUID

The characterization of Zinc oxide nanoparticles were done by XRD, SEM, EDXA and KD2 Pro thermal analyzer. Using the instrument PANalytical X’Pert PRO diffractometer the structural determination and estimation of crystalline size were carried out. The average size of the nanoparticle was calculated using Debye-Scherrer equation 5.1 and it was 50 nm. The image for XRD is shown in Fig 5.21.

Scanning electron microscope and energy dispersive X-ray analysis (EDXA) is done using the instrument Hitachi, model: S-3400 N for surface morphology and chemical analysis. The result showed that the zinc oxide nanoparticle is spherical in shape. The presence of Zn and O elements are confirmed. The thermal conductivity is measured using KD2 Pro thermal analyzer, Decagon Devices, Inc., USA. The value is found to be 0.601W/mK which showed an increase of 2.3% when compared to DI Water (0.613 W/mK).
Fig. 5.21. X-Ray diffraction pattern of ZnO

Fig. 5.22. SEM micrograph of (5000X) ZnO nanoparticles
5.13. SUMMARY

In this chapter the fabrication of the experimental setup and mounting of pressure gauges and thermo couples on the system were present. The preparation methodology and characterization techniques for nano fluids along with the critical issues were discussed in detail.
6.1. INTRODUCTION

This chapter deals with the experimental procedure adopted, relevant parameters during the course of the present investigation. In developing country like India, most of the vapour compression based refrigeration, air conditioning and heat pump systems continue to run on halogenated refrigerants due to its excellent thermodynamic and thermo-physical properties apart from the low cost. However, the halogenated refrigerants have adverse environmental impacts such as ozone depletion potential (ODP) and global warming potential (GWP). Hence it is necessary to look for alternatives refrigerants to full fill the objectives of the international protocols (Montreal and Kyoto) and to satisfy the growing worldwide demand.

6.2. BLENDING OF R152a AND R134a

The system was charged with the help of charging system and evacuated with the help of vacuum pump to remove the moisture. After charging each refrigerant, data were collected and different evaporator temperatures using equation 3.1 to 3.7. The following parameters were obtained using the above equations. a) vapour pressure b) compressor input power c) co-efficient of performance d) volumetric cooling capacity and e) pressure ratio. Initially a performance test is made with the system loaded with pure R134a. The data is treated as the basis for the comparison with the refrigerant mixtures. The mixture composed of R152a and R134a was considered as an alternative to R134a. This mixture is further referred in this work as HCM. Blend mixtures HCM of R152a and R134a by mass in the proportion of HCM 30:70 (30% weight of R152a and 70% weight of R134a), HCM 50:50 (50% weight of R152a and 50% weight of R134a) and HCM 70:30 (70% weight of R152a and 30% weight of R134a) were charged through the charging port in the compressor and the performance tests were conducted. The results of the performance
comparison of the investigated mixture of the refrigerants (R15a and R134a) in the vapour compression refrigeration system are given below.

6.3 VARIATION OF DISCHARGE TEMPERATURE

Akhilesh Arora et al., (2009) explained that the compressor discharge temperature determines the grade of insulation for the compressor and motor assembly when using refrigerant mixtures. It is clear from the Fig.6.1 that the discharge temperature increases the variation of increase in time. The discharge temperature was found to be highest for R152a followed by HCM 30:70, HCM 50:50 and HCM 70:30. The discharge temperature was lowest for the HCM mixture of 70:30, which would be appropriate from the viewpoint of system reliability and fluid stability.
Fig. 6.2 shows that the discharge pressure decreases with the variation in time. The discharge pressure was recorded to be highest for R152a followed by HCM 70:30, HCM 50:50 and HCM 70:30. The discharge pressure was found to be lowest for pure R134a.
6.5. EFFECT OF EVAPORATOR TEMPERATURE ON VAPOUR PRESSURE OF THE REFRIGERANTS

Fig. 6.3 Variation of vapour pressure with varying evaporator temperature for R152a, HCM mixtures and R134a

The variation of saturation pressure of a function of evaporator temperature for three refrigerant mixtures is shown in Fig.6.3. R152a as lowest pressure and R134a recorded the highest pressure. The HCM 70:30 recorded the lowest pressure among the three mixtures. Refrigerant with low pressure is desirable in the system because the higher the pressure the heavier must be the equipment parts and accessories. Usage of R152a owing to the lowest vapour pressure reduces the heaviness of the various components of the refrigeration system.
6.6. VARIATION OF PRESSURE RATIO

Fig. 6.4 Variation of pressure ratio with varying evaporator temperature for R152a, HCM mixtures and R134a

Pressure ratio is the ratio between outlet pressure and inlet pressure of the compressor unit. Fig.6.4 shows the variation of the pressure ratio with varying evaporator temperature for R152a, HCM mixtures and R134a. It is evident from the Fig. that pressure ratio decreases with increase in evaporator temperature. The trends are similar for the three HCM mixtures. The average pressure ratio for HCM 70:30 was lowest among the three HCM mixtures. The pressure ratio is less the compressor can be a lighter one. The same compressor can be used for the HCM mixtures.
6.7. VARIATION OF COMPRESSOR INPUT POWER

The changes of compressor input power with evaporator temperature are illustrated in Fig. 6.5, which reviews that the compressor input power increases as the evaporator temperature increases. The power consumption the compressor was found to be lesser for HCM 70:30 among the three HCM mixtures.

Fig. 6.5 Variation of Compressor input power with varying evaporator temperature for R152a, HCM mixtures and R134a
The difference in evaporator temperature was found to be in increasing trend for all the HCM mixtures with increase in time. Among the mixtures HCM 70:30 shows the highest difference in temperature which shows the higher removal of heat from the evaporator unit. The temperature difference was highest for R152a. as shown in Fig. 6.6.
6.9. EFFECT OF EVAPORATOR TEMPERATURE ON VCC

Fig. 6.7 Variation of volumetric cooling capacity with varying evaporator temperature for R152a, HCM mixtures and R134a

Volumetric cooling capacity (VCC) is the refrigerating effect per unit volume fluoride and the inlet of the compressor (B.O. Bolaji, 2011). Fig. 6.7 shows the volumetric cooling capacity with varying evaporator temperature for the three HCM mixtures. The VCC increases with increase in evaporator temperature. This is due to increase in cooling effect and decrease in specific volume, which means that the higher the VCC the smaller as the size of the compressor required. Out of the three HCM mixtures, HCM 70:30 has got higher volumetric cooling capacity. Hence a smaller size of compressor is sufficient for HCM 70:30 when compared to pure R134a.
By the first law of thermo dynamics, the measure of performance of the refrigeration cycle is the co-efficient of performance (COP). It is the refrigerating effect produced per unit of work required (B.O. Bolaji, 2011). Fig.6.8 shows the variation of COP for various HCM mixtures. Among the three mixtures HCM 70:30 as the highest COP. The lowest COP among the mixtures was as shown by HCM 30:70.
6.11. SUMMARY

In this chapter the performance of three HCM mixtures in the vapour compression refrigeration system were investigated experimentally and compared. Out of the three HCM mixtures, HCM 70:30 offers desirable characteristics such as low operating temperature and pressure, high volumetric cooling capacity and high co-efficient of performance.
CHAPTER 7

NANOADDITIVES IN R152A REFRIGERANT

7.1 INTRODUCTION

The rapid advances in nanotechnology have lead to emerging of new generation heat transfer fluids called as nanofluids. Suspending nano sized particles (1-100 nm) in the conventional fluids possess higher thermal conductivity than the base fluid. This concept is being adopted in the work of suspending nanoparticles in the refrigerant R152a. R152a refrigerant is a nature friendly used in refrigeration system. The thermophysical properties and convective heat transfer nature of refrigerant determines the performance of refrigeration equipments such as domestic refrigerators and air conditioners. The addition of nanoparticles to the refrigerant results in the improvement of thermophysical properties and heat transfer characteristics of the refrigerant thereby the performance of the system could be improved to a large extent (N.Subramani et al., 2011).

7.2 NANOADDITIVE IN VAPOUR COMPRESSION REFRIGERATION SYSTEM

Nanoparticles can be used in refrigeration system because of its remarkable improvement in thermophysical and heat transfer capabilities to enhance the performance of the refrigeration system. In a vapour compression refrigeration system the nanoparticles can be added to the lubricant oil in the compressor. When the refrigerant is circulated through the compressor it carries traces of lubricant and nanoparticles mixture (nanolubricant) so that the other heat transfer components will have nanolubricant-refrigerant mixture.

Some investigators have conducted studies on the effect of nanoparticles in the refrigerant / lubricant on the system performance. Bi et al. (2011) conducted an experimental study on the performance of a domestic refrigerator using TiO$_2$ – R600a nanorefrigerant as working fluid. They reported that the system worked safely and
efficiently with an energy saving of 9.6%. They also cited that the freezing velocity of nano-refrigerating system was more than that of pure R600a system.

Bi et al. (2007) conducted studies on the domestic refrigerator using nanorefrigerant. In their studies they used R134a as the refrigerant. TiO$_2$ nanoparticles were suspended in the mineral oil of the compressor unit. It was reported that the refrigeration system worked safely without any system modification and the energy consumption reduces by 21.2%.

Jwo (2009) conducted studies on a refrigeration system replacing R134a refrigerant and polyester lubricant with a hydrocarbon refrigerant and mineral refrigerant. The mineral oil included added Al$_2$O$_3$ nanoparticles to improve the lubrication and heat transfer performance. Their study explained that 60% R134a and 0.1% wt Al$_2$O$_3$ nanoparticles were optimal. The power consumption was reduced by 2.4% and the coefficient of performance was increased by 4.4%.

From literature, oxide nanoparticles of concentrations less than 0.5%v have shown proven enhanced thermal conductivity than the base fluids. Higher concentration of oxide nanoparticles turns to be more of insulator. Hence the concentration of nano additives namely ZnO, Al$_2$O$_3$ and CuO in this work was taken in the order of 0.05%v, 0.1%v and 0.15%v .The lubricant oil blended with the three nanoadditives was loaded in the compressor. The setup was charged with 150 gm of the working fluid R152a and the performance tests were conducted as per standards (Wong wises et al., 2005). Tests were conducted with three concentrations of the three nanoadditives in the system. The suction temperature, discharge temperature, suctions and discharge pressures were noted. The power consumption was calculated with the help of digital watt-hour meter. The performance parameters of the system computed are refrigerating effect, compressor work input, co-efficient of performance, volumetric cooling capacity and pressure ratio.
7.3 EFFECT OF CONCENTRATION OF NANOADDITIVES

7.3.1 Influence of nanoadditive concentration on vapour pressure

![Graph showing the variation of vapour pressure with 0.05% concentration of three nanoadditives.]

**Fig. 7.1** Variation of vapour pressure with 0.05% concentration of three Nano additives

![Graph showing the variation of vapour pressure with 0.1% concentration of three nanoadditives.]

**Fig. 7.2** Variation of vapour pressure with 0.1% concentration of three nanoadditive
Fig. 7.3 Variation of vapour pressure with 0.15% concentration of three nano additives

Fig. 7.1 to Fig 7.3 shows the variation of the saturation pressure as a function of the evaporator temperature for the three nano additives. Refrigerant with low pressure is desirable in the system because higher the vapour pressure, the weight of the equipment parts and accessories increases. Increase in concentration of nano additives reduces the vapour pressure of the refrigerant. The vapour pressure generally increases with the increase in the evaporator temperature. The vapour pressure curves of 0.05% concentration are nearly overlapping with each other. Addition of nano additives shows a decrease in the vapour pressure when compared to pure R152a. CuO nano additive with R152a shows a lowest vapour pressure among the other additives. Following CuO nano additive, Al₂O₃ and ZnO has higher vapour pressure. The vapour pressure of 0.1% of CuO with R152a was lowest among all the curves and it could be suggested for lighter component of the refrigeration system. 0.1% CuO with R152a has the lowest pressure with the mean pressure of 7.23% lower than that of pure R152a.
7.3.2 Influence of nanoadditive concentration on pressure ratio

Fig. 7.4  Variation of pressure ratio with 0.05% concentration of nano additives

Fig. 7.5  Variation of pressure ratio with 0.1% concentration of nano additives
M. Mohanraj et al. (2009) defined pressure ratio as the ratio of outlet pressure to the inlet pressure of the compressor. The variation of pressure ratio with evaporator temperature for the nano additives is shown in Fig. 7.4 to Fig. 7.6. Usage of nano additives shows a decreasing trend on the pressure ratio of the system. The pressure ratio decreases for ZnO followed by Al₂O₃ and CuO. Among the three nano additives CuO shows the lowest pressure ratio. The pressure ratio decreases for 0.05% and 0.1% of the nano additives but there was an increase in the pressure ratio for 0.15% concentration of the nano additives. Increase in the pressure ratio for 0.15% concentration of nano additives signifies that power consumed by the compressor unit will be more. Hence 0.05% and 0.1% concentration of nano additives will consume less power. The average lowest pressure was 3.6 which is 12.3% lower than the 0.05% concentration of CuO nano additive. More over the volumetric efficiency for 0.1% concentration is expected to be better because of relatively low pressure ratio than the other nano additives.
7.3.3 Influence of nanoadditive concentration on compressor input power

**Fig. 7.7** Variation of compressor input power with 0.05% concentration of nanoadditive

**Fig. 7.8** Variation of compressor input power with 0.1% concentration of nanoadditive
The changes of compressor input power with evaporator temperature for the nano additives are illustrated in Fig. 7.7 to Fig. 7.9. The average compressor input power for 0.1% nano additive of CuO was 9.5% lower than 0.05% of CuO and 23.7% lesser than pure R152a refrigerant. Usage of 0.1% concentration of CuO with R152a is suggested for lower power consumption. There was an increase in power input to the compressor by 2.63% with 0.15% concentration of nano additives.
7.3.4 Influence of nanoadditive concentration on volumetric cooling capacity

**Fig. 7.10** Variation of volumetric cooling capacity with 0.05% concentration of nano additives

**Fig. 7.11** Variation of volumetric cooling capacity with 0.1% concentration of nanoadditive
B. Bolaji et al. (2011) defined volumetric cooling capacity as the refrigerating effect per unit volume flow rate at the inlet of the compressor. The volumetric cooling capacity was found to increase for the addition of nano additives. Fig. 7.10 to Fig. 7.12 represents the variation of VCC with evaporation temperature. The increase in evaporation temperature causes increase in saturation pressure and decrease in specific volume at the compressor inlet. Moreover the cooling capacity also increases with increase in the evaporation temperature. The combined effect of these two factors leads to increase in VCC for the concentration of nano additives in the refrigerant under consideration. The VCC for 0.1% CuO was found to be 3.7% higher than that of 0.05% CuO, which is 22.3% higher than pure R152a. This is due to the low specific volume of 0.1% CuO with R152a which means the size of the compressor requirement would be smaller in size. At higher VCC the compatibility problem between refrigerant, lubricant and the material of system and compressor are expected to be lesser which means the expected life of the compressor for 0.1% CuO shall be higher when compared to pure R152a.

**Fig. 7.12** Variation of volumetric cooling capacity with 0.15% concentration of nano additives
7.3.5 Influence of nanoadditive concentration on COP of the system.

Fig. 7.13 Variation of COP with 0.05% concentration of three Nanoadditive

Fig. 7.14 Variation of COP with 0.1% concentration of nanoadditives
The variation of coefficient of performance (COP) with the varying evaporator temperature for the three nano additives is specified in Fig. 7.13 to Fig. 7.15. The COP increases as the evaporator temperature increases because of increase in evaporation temperature due to increase in cooling capacity in reduction in power consumed by the compressor. The COP for 0.1% CuO is highest among the other nano additives with COP of 5.1. The COP increases with the 0.1% CuO nanorefrigerant due to faster brownian motion of nanoparticles in the lubricant than the other two nanorefrigerant. This motion along with the nanoparticles along a line enhances the heat transfer coefficient. Comparison of the three nano additives reveals that ZnO nano additive gives lesser COP of 4.6, 4.62 and 4.61 with 0.05%, 0.1% and 0.15% concentration. The decreasing order of nano additives on the basis of COP can be given as CuO, Al₂O₃ and ZnO.
7.4. SUMMARY

In this chapter the influence of three nano additives namely CuO, Al$_2$O$_3$ and ZnO with 0.05% v, 0.1% v and 0.15%v concentration on the system performance parameters like vapour pressure, volumetric cooling capacity, compressor input power and COP were computed and analysed. Out of three nano additives 0.1% v CuO exhibited better system performance than the other nano additives with other concentrations. No system modification was required for the usage of nano refrigerant in the system. Good miscibility and stability of CuO nano fluid was obtained for 0.1%v concentration. From the present investigation, addition of nano particles in the refrigerant as proved to improve the system performance and less energy consumption.
CHAPTER 8
INFLUENCE OF SURFACTANT ON SYSTEM PERFORMANCE

8.1 INTRODUCTION

Surfactants are organic compounds that lower surface tension between two liquids or between a liquid and a solid. In an anionic surfactant the hydrophilic (Head) group bears a negative charge and in a cationic surfactant the hydrophilic (Head) group bears a positive charge. The critical micelle concentration (CMC) is defined as the concentration of surfactants above which micelles are formed and all additional surfactants added to the system go to micelles. Above CMC value the monomers form a flower shaped micelles.

8.2 EFFECT OF AGGREGATION ON THERMAL PROPERTIES OF NANOFLOUIDS

Wu.C et al. (2010) recently reported in their experimental studies that the formation of local nanoparticles aggregation can play a significant role in the thermal transport in nano fluids.

Hong TK et al. (2005) demonstrated that Fe nanoparticles in the Nanofluids can locally assemble into aggregate of micron sized clusters. The aggregation can be controlled by surface charge and the critical importance of particle surface charge in nano fluids thermal conductivity was demonstrated by Lee et al. (2006).

Rajesh Kumar Neogy and Arup Kumar Raychaudhuri (2013) investigated the effect of adding a stabilizer on the dynamic thermal properties of ZnO nano fluid (containing 5 to 10 nm diameter of ZnO nano crystals measured using a 3ɷ method. They reported that addition of stabilizer lead to the stabilization of the nanofluid and a substantial reduction of the enhancement of the thermal properties when compared to bare ZnO nanofluid was noted. They suggested that the addition of the stabilizer inhibits the thermodiffusion-assisted local aggregation thus leading to substantial reduction of the enhancement of thermal properties.
In the present work two types of surfactants namely Sodium dodecyl sulfate (SDS) an anionic surfactant and Cetyltrimethyl ammonium bromide (CTAB) a cationic surfactant were added to the compressor oil at their CMC values and the COP was investigated. The CMC values of SDS and CTAB are 1.2 g/L and 1.6 g/L respectively. The system performance was found to be better with 0.1% concentration of nano additives than 0.5% and 0.15% from the earlier chapters. Hence at 0.1% concentration of nano additives, both the surfactant were added at CMC values and their respective COP of the refrigeration system were investigated.

8.3 INFLUENCE OF CTAB ON COEFFICIENT OF PERFORMANCE.

Addition of CTAB at CMC value of 1.6g/L lowered the COP values with 0.1% concentration of nano additives. For CuO the COP value dropped from 5.1 to 4.7 (7.8%) for Al₂O₃ the value reduced from 4.87 to 4.34 (10%) and for ZnO the value of COP reduced from 4.76 to 4.21 (11.56%). Hence it is evident that addition of CTAB surfactant with the nano refrigerant has reduced the performance of the system.
8.4 INFLUENCE OF SDS ON COEFFICIENT OF PERFORMANCE.

Addition of SDS at CMC value of 1.2g/L also shows a decreasing trend of COP with 0.1% concentration of nano additives. For CuO the COP value dropped from 5.1 to 4.5 (11.76%) for Al₂O₃ the value reduced from 4.87 to 4.2 (13.7%) and for ZnO the value of COP reduced from 4.76 to 4.1 (13.8%). Hence it is also evident that addition of SDS surfactant with the nano refrigerant has also got reducing characteristic feature on the performance of the system.

**Fig.8.2** Influence of SDS on COP with 0.1%v of nano additives
The addition of surfactants showed a negative effect on the COP of the system. It is evident from the Fig.8.3 that addition of surfactant CTAB and SDS has reduced the COP of the system. On comparison between the two surfactants, SDS (anionic surfactant) has got higher pulling down effect on the COP of the system than CTAB (cationic surfactants). From Fig.8.3 it was noted that there is a reduction in COP between and CTAB and SDS by 4.25%. Hence it is concluded from the investigation that addition of surfactant with the nano refrigerant reduces the system performance.

8.5 SUMMARY

In this chapter the influence of surfactants namely SDS and CTAB at CMC on the COP of the system was investigated and presented. The results showed reduction in COP with the addition of the surfactants. It is also clear from the results that SDS has more influence than CTAB in the reduction of the COP of the system.
CHAPTER 9

CONCLUSIONS AND SCOPE FOR FUTURE WORK

9.1 CONCLUSIONS

An experimental study was conducted in chapter 6 with the blend of R152a and R134a in vapour compression refrigeration system. Based on the present investigation, the following specific conclusions could be drawn.

- The discharge temperature and the discharge pressure of the compressor were found to be lowest for HCM 70:30 when compared with other mixtures.
- HCM 70:30 recorded the lowest vapour pressure among the mixtures which reduces the heaviness of the components of the refrigeration system by using this blend.
- The average pressure ratio for HCM 70:30 was lowest with the value of 4.3 which promises the life extension of the compressor.
- The average input power to the compressor for HCM 70:30 was found to be 9.5% lower than R134a. Usage of this blend reduces the power consumption of the system.
- The heat removal rate was higher for HCM 70:30.
- Higher volumetric capacity of 4.9% higher for HCM 70:30 was observed when compared to other blends of refrigerants. This ensures increasing cooling effect for the same size of the compressor as used for pure R134a.
- Highest COP value was obtained for HCM mixture 70:30.
- The system works safely with the replacement of R152a blend with the conventionally used R134a.
- No system modification was done for the retrofitting process which is a major advantage of the present research.
Based on the experimental results conducted in chapter 7 the following conclusions have been drawn from the usage of nano refrigerants. For the first time investigation was made on the influence of nano additives in R152a refrigerant. The results showed that after adding nano additives to refrigerant the performance of refrigeration system was significantly improved. The results also reveal that ZnO, Al$_2$O$_3$ and CuO nano refrigerant works normally and safely in the system. The usage of R152a has zero Ozone Depleting Potential (ODP) and very less GWP and thus provides a Green and Clean environment. Based on the investigation the following conclusion could be drawn.

**A. On vapour pressure**

- Addition of nano additives with R152a decreases the vapour pressure of the refrigerant. Nano refrigerant with low vapour pressure will desirable the system as it reduces the weight of the components of the system and its accessories. The vapour pressure of 0.1% CuO was found to be lowest with the mean pressure of 7.23% lower than pure R152a.

**B. On pressure ratio**

- The pressure ratio decreases with the addition of nano additives. The average lowest pressure was 3.6 for 0.1% CuO which 12.3% lower than 0.5% CuO. Decrease in pressure ratio improves the life of the compressor.

**C. On compressor input power**

- The compressor vapour pressure was found to decrease on the addition of nano additives. The average compressor input power for 0.1% CuO was 9.5% lower than the other concentration and other nano additives. This value is 23.7% lesser than pure R152a refrigerant.
D. On volumetric cooling capacity

- The addition of nano additives facilitates the improvement in cooling capacity. The VCC for 0.1% CuO was found to be 3.7% higher than that of 0.05% CuO which is 22.3% higher than pure R152a. This is due to low specific volume at 0.1% CuO which reduces the size of the compressor requirement. This higher value of VCC the compatibility problem between refrigerant, lubricant and compressor material could be higher.

E. On COP of the System

- Increase in evaporation temperature due to the increase in cooling capacity improves the COP of the system with the reduction in power consumption of the compressor. The COP of 0.1% of CuO is found to be highest among the other nano additives. The decreasing order of nano additives on the basis of COP can be given as CuO, Al₂O₃ and ZnO. Thus the usage of 0.1% CuO nano additive with R152a which has low GDP value of 140 and zero ODP ensures safe and clean environment with less power consumption.

- Addition of both surfactants SDS and CTAB shows lowered value of COP than the addition of nano additives in the refrigerant R152a.

9.2 SCOPE FOR FUTURE WORK

❖ The following are the important future research needs with respect to environment friendly alternative refrigerants:

(a) Hydro carbon refrigerant will be considered as a long-term alternative for halogenated refrigerants which are flammable. Hence development for new refrigeration system with low refrigerant inventory is essential.
(b) Very limited pure alternatives are available. Therefore, the new refrigeration system designs should accommodate the non-linear property variation of environment friendly mixed refrigerants.

(c) Compatibility of the alternative refrigerants mixtures with lubricants and the construction materials is required to be studied further.

(d) Inert nature of hydrocarbons with hydro fluoroarbon refrigerants needs further investigation.

(e) An environmental property of new refrigerant mixtures also needs further investigation.

- The heat transfer results show that nano fluids have significant potential for improving the flow boiling heat transfer of refrigerant/lubricant mixtures. However, the reasons behind this marked improvement with nano particle volume fractions at different concentrations are not clearly understood. It is unclear why a large increase in heat transfer is observed with a insignificant increase in pressure. Moreover, obvious challenges with particle circulation and unknown effects on the compressor of an air conditioning or refrigeration system have not been addressed. Nevertheless, the present findings are compelling and further research should be undertaken.

- Future research is required to investigate the influence of the particle material. Its shape, size, distribution, and concentration on refrigerant boiling performance.

- Experimental results on the fundamental properties such as specific heat, density, and viscosity of nano fluids are very limited in the literatures. There are potentials to explore research to determine these properties experimentally.

- In the present study typical anionic and cationic surfactants were used improve the performance of the refrigeration system. Other types of surfactants such as Zwitterionic which contains a head with two oppositely charged groups positive and negative could be tried out.
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