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# Ultrasonic thermophysical enhancement of a novel nanodoped vapour compression fluid for high cooling efficiency



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# ABSTRACT

In refrigeration systems, a pertinent problem hunting efficient energy recovery is one ascribed to low thermal conductivities of the compressor oil and coolants. Hence, in this study, copper and silicon nanoparticles were synthesized via advanced techniques and used to induce higher heat conductivities/electrical potentials in a compressor oil so as to impose effective interactions between the molecules of the nano-compressor oils sonicated at varying frequencies towards achieving high performance and energy conversion when used with R134A. The results of the SEM-EDX images received for the CuNPs and SiNPs confirmed the formation of circular copper and silicon nanoparticles of average particle sizes ranging from 2 to 7.1 and 3.35-29.35 nm for Cu and Si respectively. It was also observed that particle concentration and sonication speed of the sonicated lone and combined/hybrid nanoparticle entrained oils had significant influence on the cooling effects and coefficients of performance of the refrigerator. In addition, the 1 M CuNP- and 0.56 M SiNP-oils gave the best cooling effects with temperatures of about -11 °C and -7°C respectively at a pull down time and frequency of 18000 s and 120 kHz respectively.

#### Introduction

The energy demands of commercial and industrial refrigeration systems have gained continuous increase over time. Hence, the application of nanotechnology in refrigeration involves the use of engineered nanoscale materials with promising potentials for influencing the performance of refrigeration systems towards ensuring efficient cooling and expansion with bearable or insignificant consequences (low/no ozone depletion/global warming potentials and high environmental tolerance). Nanoparticles are either mixed with compressor lubricating oils or refrigerants as a way of ensuring high performance or improved refrigeration with reduced tendencies for erosion or friction in the moving parts [1]. In refrigeration systems, lubricated moving parts ought to be tenacious with good adherence to long-lasting shear-resistant surface films for the duration of the machine's life [2]. In essence, nanoscale lubrication for high-friction regulation and adhesion requires that non-volatile, heat-resistant lubricants with strong adhesive properties including stability, self-repair characteristics and self-generating capabilities are used with slight modifications [3]. Nanofluids can be made via one and two-step techniques i.e., by straight run vapourcondensation and suspension of the particles in the oil, while the other entails producing the nanoparticles, followed by their subsequent dispersion in the oil [4]. The most important thing to note here is that particle-agglomeration or clustering must be avoided since either of these can block miniaturized channels as well as reduce the ability of the fluid-particle system to conduct heat [5,6]. In lieu of the fact that the use of nanofluids is fast gaining attention, their application in energy systems is limited owing to the inherent high pressure drop, poor thermal conductivity, low thermal capacity, particle settling and high pumping power [7], hence the need to look into optimizing the potentials of these systems for improved system performance. This is achievable via several alternatives including the apt selection of the required nanoparticulate precursors, method of nanoparticle synthesis, choice of surfactants as well as the moderation of process parameters such as sonication power, speed, frequency, mode of operation etc., hence, the motivation for this study.

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Received 10 January 2022; Received in revised form 1 August 2022; Accepted 22 September 2022 Available online 28 September 2022 2451-9049/© 2022 Elsevier Ltd. All rights reserved. Thermal conductivity is a very important property of nanofluids in cooling systems which helps in improving their heat transfer efficiencies. The coefficient of heat transfer and heat transfer-rate in such systems strongly depend on the thermal conductivities of the nanofluids which are influenced by several parameters including particle-volume fraction, temperature, particle size, particle shape, pH, type of additive as well as degree of sonication. The low thermal conductivity of nanolubricants makes them more susceptible to vapourization and condensation. Jiang et al. [8] determined the thermal conductivity of nanofluids is greatly affected by nanoparticle-clusters and their shapes. The mixing of nanoparticles in the oils can be achieved via sonication which supplies a certain amount of sound energy to the solution within a specific sonication time and frequency that is adequate for particle-dispersion in the medium [9,10].

The operation of a refrigeration system is in accordance with the second law of thermodynamics (the total entropy of an isolated system will not decrease over time but remains constant if and only if the entropy-generation process is reversible). Refrigeration as a process, helps to expel heat from a substance (refrigerant) in an encasement, in order to lower the temperature via expelling warm air from the lowtemperature repository to a high-temperature system [11]. Nano lubricants used in refrigeration systems are lubricants doped with nanometer-sized particles which act as additives and in turn transfer uniquely interesting tribological properties to the fluids [12-14]. To protect the surfaces of the particles, it is important to control and maintain their surface energies/electrostatic charges, as well as their defects and active sites with surfactants. Literature has it that, without surfactants, the macro-scale squeezed liquid film mechanism does not provide the desired surface-charge due to lack of minimal regulation of the contact geometry as well as the insufficient number of molecules forming the films.

Till date, refrigeration systems have not been optimally utilized in situations where variations in parameters are taken into consideration during sonication. In this research prospective, variations in parameters like frequency, power, energy, entropy etc. were considered in relation to how they affect the performance of a refrigeration system all aimed at determining the most ideal conditions for high performance of such systems. Refrigeration systems consume more energy than other devices [15]. Environmental impacts of refrigerants include ozone depletion, environmental degradation as well as potential harm to humans caused by the assimilation of the expelled gases during compression. Thus, as a way of minimizing their environmental impacts, compressor oils are often nano-doped via sonication. During sonication, the inherent intermolecular forces of the fluid help to accelerate particle-dissolution [16]. The resulting sound waves are then propagated through the liquid medium at high/low alternating pressure cycles at frequencies usually within the range of 20-40 kHz; this also serves as the motivation for this research where higher frequencies were explored in order to determine their effects on the performance of a refrigeration system. Microscopic vapor bubbles ensue during very low-pressure cycles, and thus may result in a situation known as cavitation, whereas, in the high-pressure regions, there exists the generation of bubbles which rupture/burst, thus producing a localized shockwave which releases substantial amounts of mechanical and thermal energies [17]. Ultrasonicators convert electrical energy from a transducer into vibrational energy thus causing the fragmentation of the suspended particle clusters [18]. This is made possible by the inducement of extreme localized temperatures and pressures produced by the interaction of reactive species within the sonication medium; this also pricks the creation/availability of covalent bonds on the nanoparticles' surfaces. However, if organic molecules are present in the medium during sonication, nanoparticle suspensions which assume the form of homogeneously dispersed particles with surface coats in a liquid medium may irreversibly become degraded via direct sonlysis [17]. Viscosity being another very interesting thermophysical property of thermo fluids reduces their inherent heat transfer

potentials and pressures. With an increase in the dynamic viscosity of nanofluids, the convective heat transfer coefficient and frictional pressure decrease with a resultant increase in the fluids pumping power. Mahbubul et al. [19] conducted an investigation to assess the impact of volume fraction and temperature on the viscosity of nanolubricants on different refrigerants (R134a, R141b and R123); they observed that the viscosity of the nano-lubricants decreased with nanoparticle concentration and temperature rise. The viscosity and thermal conductivity of a fluid can be influenced by adding micrometer or nanosized particles to the base fluid [20,21]. Nano-fluids are prepared as heat exchanging liquids by homogenizing stable nanometer-sized solid particles in liquids/oils [22]. The thermal exchange of the nano liquids is much higher than those of unadulterated liquids, provided that the ultrafine particles are suspended significantly in the fluid thus increasing the mixture's heat conductivity with a resultant increase in heat exchange efficiency [23].

Refrigeration is an artificial process by which a substance/system is brought from a higher temperature to a lower or sustainable temperature below ambient conditions by heat exchange [24,25]. For this to be achieved, the refrigerant is pumped through an enclosed space such that it flows and disperses into the compressor oil. However, since the system is a closed loop, the refrigerant is recycled as it goes through the cycle, thus removing and releasing the acquired heat. There are also oils that have high compatibilities with several refrigerants, however, Copeland 46B, Polyalkylene glycols (PAGs) and Polyolesters (PoES) are the most suitable oils, because they possess good miscibility with modern alternative refrigerants and have good electrical insulation which is critical for efficient compression [26]. The aforementioned mineral oils can be mixed/sonicated with nanoparticles for improved fluid properties and synergistic energy maximization. Via ultrasonication, energy is released at inaudible frequencies i.e., at frequencies >20 kHz in order to induce vibration, mixing as well as ease the separation of particle-agglomerates through a process known as cavitation [27]. Nanoparticles possess several physical and optical properties that bring about their total quantum effects which impact directly or indirectly on the overall performance of energy systems. Besides their abilities to improve energy utilization, their confinement as conductors/semi-conductors as well as their high surface areas to volume ratios provide for their increased diffusion potentials at high temperatures with no known negative effects on humans, plants and the environment [28]. Amongst the available types of nanoparticles used in refrigeration systems, copper stands out owing to its: incredible conductive/tunable surface properties, minimal production costs, rare surface resonance, reactivity/compatibility with polymers [29], alongside its evident-thermal and electrical conductivities [30], hence the reason for its consideration for use in managing the temperature of liquids used in electrical frameworks [26] with sizes ranging from 1 to 100 nm [31]. Copper nanoparticles can be produced by natural or synthetic approaches such as the chemical reduction method [32]. Often times, the metal becomes oxidized or debased to its oxide(s) because of its high affinity for air; this then suggests the need for caution when handling the metal, especially when the desire is to use the metal in its non-oxidized form [17]. CuNPs have shown promising potentials in areas such as the production of antimicrobial agents/nanofluids, making of electrical/conducting films and blending of lubricants [33,34]. Their developmental stages entail the addition of ascorbic acid solution in a synthetic medium [35]. The synthesized nanoparticles are then stabilized with surfactants which also assist in controlling the size and shape of the resulting nano-particulates. Also, the choice of precursor-salt and solution-pH go a long way to influence the properties of the resulting nanoparticles [17]. Another type of nanoparticle that has promising potential in improving the performance of energy systems is that of silicon which is produced via the colloidal method and possesses unique catalytic, magnetic and optical properties; the particles are usually in the form of dark brown round bodies/spheres with high surface areas [36]. They have the ability to absorb electromagnetic waves. Isolated Si-nanoparticles are often very difficult to synthesize without a

surfactant, because of the high forces of attraction that exists within the particles.

Some related works on the subject include: the work of Hu et al. [37] that presents the properties and behaviour of a nucleate pool boiling heat transfer refrigerant/nano-lubricant mixed with three surfactants (SDS- anioinic surfactant, CTAB- cationic surfactant and Span-80- nonionic surfactant). Based on the results, the nanolubricant's (VG68 and Cu nanoparticles) heat transfer coefficient ratio of refrigerant/nanolubricant-surfactant mix to that void of surfactant was in the range of 0.85-1.58, 0.73-1.31, and 0.68-1.24 for the SDS, CTAB and Span-80, respectively. These values were seen to increase initially with surfactant concentration and then decrease afterwards, thus suggestive of an optimum concentration, whereas, it increased for a decrease in surfactant-molecular weight, nanolubricant concentration and heat flux. Javadi and Saidur [28] observed the environmental and energy conservation effects of a nanorefrigerant used in a domestic refrigerator. They used R-134a refrigerant alongside different mass fractions of TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> nanoparticles. Their findings revealed that more energy can be conserved using 0.1 % TiO<sub>2</sub> nanoparticle mixed with mineral oil as compressor fluid alongside the refrigerant, and the reduction in energy consumption can be about 10,863 MWh with lower CO<sub>2</sub> emissions by the year 2030. The work of Padmanabhan and Palanisamy [38] involved the use of TiO<sub>2</sub> nanoparticles in a vapour compression refrigeration system (VCRS) which helped to reduce the level of irreversibility exhibited by the refrigerator. Alawi and Sidik [39] determined the thermophysical properties and heat transfer performance of 1,1,1,2-tetrafluoroethane (R-134a)-CuO (1-5 vol%) suspension in a refrigeration system. Based on their findings, the thermal conductivity, specific heat of the nano-CuO/R-134a, viscosity and density increased with increased particle concentration/vol%, whereas, the properties decreased with temperature, thus suggesting an optimal particle volume fraction for improved performance. Jiang et al. [40] mentioned that refrigerantbased nanofluids exhibit higher thermal conductivities relative to nonnano-entrained refrigerants. Also, some other authors have justified the improved performance of refrigeration systems using refrigerantbased nanofluids as compared to those of pristine/pure refrigerants [41–43]. However, the aggregation and sedimentation of nanoparticles in refrigerant-based nanofluid may reduce the stability of the fluid, thus limiting its application in refrigeration systems. Alawi et al. [44] conducted a review on the thermophysical properties of nanoparticles suspended in refrigerants and lubricating oils. They also discussed the effects of nano-lubricants on boiling two phase flow phenomena. Their conclusion was that nano-refrigerants are more temperature-dependent thus exhibiting higher thermal conductivities at very low particle concentrations than conventional refrigerants, which in turn enhances the performance of refrigeration and air conditioning systems. They also asserted that a combined system comprising of HFC134a and polyolefin elastomer (POE) oil mixed with TiO2 nanoparticles is not only safer in terms of emission-release, but better in terms of COP-enhancement and performance, with energy saving-capacity of 26.1 % for 0.1 % mass fraction of TiO<sub>2</sub> nanoparticles in the oil relative to the system comprising of POE and HFC134a without nanoparticles. In a similar study conducted by Elcock [45], TiO<sub>2</sub> nanoparticles were used as additives to enhance the miscibility of POE with hydrofluorocarbon (HFC134a) as refrigerant. Based on their findings, refrigeration systems comprising of a mixture of HFC134a and POE-oil mixed with TiO2 nanoparticles gave better performance by returning/recycling a high volume of the lubricant to the compressor relative to the system using HFC134a and POE oil only. Lee et al. [46] applied 0.1 vol% nano-fullerene-doped mineral oil of low viscosity  $(8 \text{ mm}^2 \text{/s})$  as lubricant in a refrigerator to decrease the friction coefficient under the same or higher load-capacity. The friction coefficient of the nano-doped fluid as evaluated by a disk-on-disk tribotester decreased by 90 % relative to that of the pristine mineral oil. Kedzierski et al. [47] experimented properties such as kinematic viscosity, density, and thermal conductivity of 11 synthetic polyolesterbased nanolubricants mixed with surfactants of varying concentrations

within the temperature range of 288–318 K at atmospheric pressure. Spherical and non-spherical aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) and zinc oxide (ZnO) nanoparticles of varying mass fractions, with respective average diameters of 127 and 135 nm were used. Model-predictions of the nanodoped fluids' properties include kinematic viscosity ( $\pm 20$  %), thermal conductivity ( $\pm$ 1%), and specific volume ( $\pm$ 6%) as functions of temperature, nanoparticle mass fraction/diameter and surfactant mass fraction. The estimated viscosities, densities and thermal conductivities were seen to increase with increase in nanoparticle mass fraction. According to Meyer et al. [48], nanofluids can transit from being Newtonian to becoming non-Newtonian at critical shear rates. Hernandez Battez et al. [49] observed that nanofluids were Newtonian at shear strain rates less than 700  $\mathrm{s}^{-1}$  while they exhibited non-Newtonian behaviour at far higher shear rates  $(10^6 \text{ s}^{-1} \text{ to } 10^7 \text{ s}^{-1})$ . The performance of a domestic refrigerator using R134a (tetrafluroethane) as refrigerant with two separate compressor oils polyalkaline glycol (PAG) and mineral oil doped with varying mass fractions of Al<sub>2</sub>O<sub>3</sub> nanoparticles was examined by Adyanshee et al. [50]. The results showed that 0.2 % Al<sub>2</sub>O<sub>3</sub> nanoparticles increased the coefficient of performance of the system by 7.75 % and 19.38 % for the PAG and Mineral Oil-Al<sub>2</sub>O<sub>3</sub>doped lubricants respectively, whereas, for the 0.4 % Al<sub>2</sub>O<sub>3</sub> nano-doped oil, the corresponding increase in COP were 14.48 and 25.3 % for the PAG and mineral oils respectively, which reveals a 9.44 % COP-increase for the mineral oil over the PAG oil. The effects of copper (II) oxide (CuO) and copper-silver (Cu-Ag) alloy nanoparticle doped-POE on the coefficient of performance in relation to the heat release rate, friction and wear mechanism of a vapor compression refrigeration system running on HFC-R134a as refrigerant were investigated [51]. From the results, it was observed that the 0.5 vol% Cu-Ag alloy and CuO nanolubricants, gave COP increments of 20.88 % and 14.55 %, respectively compared to those of the pristine compressor oil owing to the enhanced tribological properties of the oil by the nanoparticles. The average coefficient of friction of the Cu-Ag alloy nanolubricant was 5.5 and 9.9 %lower than that of the CuO-POE and pure POE compressor oils respectively. Al<sub>2</sub>O<sub>3</sub> mixed with a refrigerant, was adopted as refrigerant in a vapour compression refrigeration system by Mahdi et al. [52]. COP increments of 3.33 and 12 % were recorded when 0.01 and 0.02 vol% Al<sub>2</sub>O<sub>3</sub> nanoparticles were blended with the refrigerant, respectively. Selimefendigil and Bingolbali [53] carried out an experimentation on TiO<sub>2</sub> nanoparticle-doped compressor oil during refrigeration with R134 used as refrigerant. The COP of the system was determined for various nano-titanium oxide concentrations and it was observed that 1 % nano-TIO<sub>2</sub> addition to the compressor oil gave a COP increment of 21.42 %. Comprehensive studies on heat transfer performance and rheological behavior of nanofuids have also been documented by Asadi and Pourfattah [54] and Alarif et al. [55]. From reports, R134a only has zero ODP but its global warming potential is approximately 1430 for a 100-year span using CO<sub>2</sub> as reference gas, which is still higher compared to that of hydrofluoro-olefins (HFOs) and hydrocarbon refrigerants (HCs). However, R134a is still in use in some countries as the major refrigerant in refrigerators. In the study conducted by Hanif and Shafie [56], the cooling process of an electrical power/refrigeration system was improved upon by exploiting via numerical simulation, the measure of interactions that exist between incorporated multi-walled carbon nanotubes (MWCNTs) in a mineral oil based Maxwell nanofuid. The MWCNTs imposed excellent thermal conductivity, faster heat transfer rate, and higher critical heat fluxes. They also considered the effects of heat radiation, viscous dissipation and Newtonian heat flow on the system. However, their findings revealed that the velocity of the fluid increased with an increase in the relaxation time parameter but decreased with values obtained for the fractional time-derivative. Ali et al. [57] conducted a systematic review on the synthetic approaches and problems associated with the use of carbon-based (carbon nanotubes, graphene, and nanodiamond-based) nanofluids and their inclusion in thermal systems commonly available in the energy sectors. Their dispersion stability were discussed in terms of measurement techniques,

enhancement methods, as well as their effects on the thermophysical properties of the suspensions. They also presented some correlations used to determine the thermophysical properties of the suspensions and assessed the influence of the aforementioned working fluids on parabolic trough solar collectors, nuclear reactor systems, air conditioning as well as refrigeration systems. Babarinde et al. [58] used varying concentrations of graphene (0.2, 0.4 and 0.6 g/L) doped in a mineral oil to produce graphene nanolubricant for the enhancement of the performance of an eco-friendly refrigerant (R600a) in a vapour compression system. The performance of the refrigerator was determined for each of the nanolubricants for 50, 60 and 70 g of R600a refrigerant and compared with a base lubricant (mineral oil). According to the results, the system performed better for the R600a-graphene nanolubricant system compared with that of the base lubricant in terms of pull-down time, COP, power consumption and cooling capacity. In another study, Babarinde et al. [59] also conducted a comparative study of the energy performance of a refrigeration system running on R600a/TiO<sub>2</sub> and R600a/MWCNT nanolubricants and observed that the integration of the hybrid systems improved the thermophysical properties of the system as well as the system's performance. A comparative study on the energy performance of R600a/TiO<sub>2</sub> and R600a/MWCNT in a vapor compression refrigeration system has also been carried out [60].

Considering the dearth observed in the current body of knowledge on the subject, where previous studies have failed to examine the comparative influence of lone silicon and combined systems of nanosilicon and nano-copper-doped compressor oils on the coefficient of performance of a refrigeration system towards improving on the energy conservation of the system in terms of the resultant cooling effect, it then became necessary to embark on this research. In this study, parametric investigation of the effects of varying sonication speed and nanosilicon/ copper on the properties of a vapour compression compressor-oil system was carried out, towards maximizing the generated enthalpies, pressure drop and entropies in the system for efficient energy management, cooling and optimized COPs.

#### Equipment, materials and method

#### Equipment and materials

The equipment and materials used include U-V spectrophotometer-7310 visible Scanning Spectrophotometer integrated with a 10  $\times$  10 mm cuvette holder, 320-1000 nm wavelength, resolution is 1 nm with an accuracy of  $\pm 2$  nm, manufactured by Jenway, Hanna pH 211 m, Three frequency (CCH-4040D-40/80/120 kHz P4 40/80/120 kHz) piezo ultrasonic transducer (220 V, 200 W, 40KHz-120KHz; power input is 30 W; resonance impedance  $<40 \Omega$ ), centrifuge (TD5-centrifuge, 250 W, 5000 rpm), Thermometer (K-type scientific digital thermometer/thermocouple DM6801), digital weighing balance (Stwart systems Pro), beaker, magnetic stirrer (Bionics Scientific India, speed is 0-1800 rpm), conical flasks, graduated/measuring cylinders, round bottom flasks, sample bottles (by J-Sil Borosilicate), spatula (stainless steel), hot plate (Digital Lab, Shanti Scientific Industries, Mumbai, India), single door (LG GC-051A, voltage is 220-220 V; defrosting technology - direct cooling with compressor spec: rated current is 3A, max input power is 260 W, storage temperature is -25-85 °C; max storage relative humidity is 85 %)-50 L LG refrigerator, while the chemicals/materials include copper (II) sulfate pentahydrate salt (AR Grade: 99 % purity, Sigma Aldrich), ascorbic acid (C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>) (AR grade: 99–100.5 % purity, LOBAChemie), deionized water, NaOH pellets (Analytical grade- 99 % purity, Raj Pellet Industries), 95 % pure NaCl (Akzo Nobel Salt, Denmark), 98-99 % pure MgCl2 of 95.21 g/mol molecular weight (Anmol Chemicals, India), 98 % pure technical grade AlCl3 (Anmol Chloro Chem, Gujarat, India),  $\geq 99\%$  pure CaPO4 (Jianan Jinquan Chemical Industry Co. ltd., China), 99 % pure  $CH_3OH$  (Dounachem GmbH, Vienna, Austia), 99.8 % pure NN- dimethyl formamide (DMF) (J.T Baker).

## Method

Cu and Si were selected as the choice nanometals for this research owing to the fact that, in modern-day research on refrigeration, lubricants doped with copper nanoparticles (CuNPs) have caught the attention of several researchers as a result of their excellent properties, and these include their relatively small particle sizes, high melting point and ductility. In addition, owing to the relative abundance of Si, its high consideration for use in modern day energy systems such as perovskites, its scarce consideration for use in refrigeration systems, its ecofriendliness at permissible concentrations, its use for medical, cosmetic, cooking and electrical purposes, are also suggestive of its potential use in energy systems, however, moderate concentrations of the metal are desired in this regard. Furthermore, from literature, Si has also been presented as a naturally occurring element that is non-toxic. The relative high melting points of Si and Cu i.e., 1414 and 1085 °C respectively also complement the reason for selecting Si and Cu for this research.

#### Synthesis of copper nanoparticles

Copper nanoparticles were prepared by chemically reducing copper (II) sulphate pentahydrate salt with starch as capping agent. To prepare 0.5 M (mol/dm<sup>3</sup>) Cu nanoparticles, 12.2 g CuSO<sub>4</sub>·5H<sub>2</sub>O was measured using a weighing balance and transferred into a 500 mL beaker. By means of a graduated cylinder, 100 mL of deionized water was measured and poured into the beaker and stirred vigorously while heating at 80 °C. A light blue solution was seen with an offensive choking smell. 105 mL of 1 M ascorbic acid solution was then added to the resulting mix with starch while continuously and rapidly stirring the mixture. A resulting colour change from light blue to dark green was seen with copper nanoparticles formed at the bottom. NaOH was then added slowly to the green solution while constantly stirring and heating it at 80 °C for 2 h. Thereafter, the solution was allowed to cool and left for 3 days to ensure complete reaction. The precipitate was then separated by filtration and washed with ethanol 2-3 times in order to remove excess starch that may have stuck to the nanoparticles' surface. The particles were then dried at room temperature and stored for further testing. The same procedure was then repeated by measuring separate masses of 24.9 g and 37.4 g of CuSO<sub>4</sub>·5H<sub>2</sub>O as the required quantities for preparing the 1.0 and 1.5 M CuSO<sub>4</sub>·5H<sub>2</sub>O precursor-concentrations for synthesizing the corresponding copper nanoparticles and the steps mentioned above were followed through to the end to obtain 1 and 1.5 M CuNPs. Fig. 1 is a flow scheme of the process-route for synthesizing the CuNPs.

#### Synthesis of colloidal silicon nanoparticles

In lieu of the technological progresses made in nanoparticles' synthesis, the development of a simple and inexpensive route for the synthesis of homogeneous silicon nanoparticles can be achieved using the approach of Shavel et al. [61]. It is a simple/inexpensive colloidal synthetic approach that ensues under normal pressure (1 atm) and mild temperature (25–30 °C) with resultant homogeneous spherical silicon nanoparticles of nanometer sizes. One major characteristic of the method is making an apt choice of: eutectic salt mixture as solvent, the right silicon alkoxide precursor as well as ensuring the use of alkali earth/group II metals as shape-controlling agent.

The recovery of a eutectic mixture of AlCl<sub>3</sub> mixed with NaCl and MgCl<sub>2</sub> is necessary for the synthesis of size controlled SiNPs. This was ensured via the following steps. At first, equal volume i.e., 50 mL of two salts (AlCl<sub>3</sub> and NaCl; 100 g of each salt was weighed using a weighing balance and added to two separate 50 mL solutions of distilled water) before being combined in a volumetric flask; the mixture was then warmed under mild condition as mentioned above. This is so as to prevent solvent loss that ensues via sublimation when AlCl<sub>3</sub> is used alone, because, AlCl<sub>3</sub> has a high vapour pressure/triple point at 193.7 °C [62]. Hence there is need to control this by the combined mixing of the salts which is characterized by a lower melting point and high stability



Fig. 1. Flow scheme for CuNP synthesis.

(at  $\sim$  500 °C). To prepare the SiNPs, a binary mixture of 50 % (250 mL) AlCl<sub>3</sub> and 50 % NaCl (250 mL) (1:1) with a melting point of 151 °C was prepared as solvent-mixture for the colloidal synthesis of the SiNPs. Due to its relatively high boiling point and stability, tetramethyl orthosilicate (TMOS) was chosen as the silicon precursor. To make 0.56 M SiNPs, 68.54 g of the silicate was added to 500 mL of the binary solution and stirred thoroughly using a magnetic stirrer; the solution was then topped to 1 L (1000 mL). A colloid-like solution then resulted with high aggregates of polydisperse particles of SiNPs. As a way of controlling the particle size/morphology, a shape and size control-agent (20 mL of 1 M CaPO<sub>4</sub>) was used to direct the asymmetric growth of silicon particles in the aqueous medium [63]. Few drops of pure (99%) methanol were then added to the resulting mix and the mixture was centrifuged at 3000 rpm as a way of ensuring size-selective precipitation. An alkali earth chloride MgCl<sub>2</sub> was also added to the centrifuged mixture as additive which gave rise to circular SiNPs after undergoing double extraction; this was done by the addition of hexane (non-polar solvent). The procedure was repeated 3–5 times such that the separate hexane aliquots were then mixed together. The residual NaCl, MgCl<sub>2</sub> and AlCl<sub>3</sub> were confined in the methanol phase with the SiNPs almost entirely visible in the hexanelayer. Finally, few drops of N—N dimethyl formamide (DMF) were added to the hexane-layer to precipitate the SiNPs. The phase/visible colour changes observed include: a non-extractable residual black insoluble fraction comprising of pure carbon alongside retained fractions of NaCl, MgCl<sub>2</sub> and AlCl<sub>3</sub>, a blue colour hexane soluble fraction entrained with polymeric products of carbonization and dark brown polydisperse nano-silicon in the polar solvent (DMF). To produce the 1.29 and 1.69 M SiNPs, the same procedure described above was repeated using 137.08 and 231.66 g of the TMOS respectively. Fig. 2 shows the flow scheme for synthesizing the SiNPs.



Fig. 2. Flow scheme for SiNP synthesis.

# Dehydration and synthesis of Nano-lubricating compressor oils

Dehydration of R134a-compressor oil. Since Copeland 46B oil is hygroscopic, the Filson filter vacuum dehydrator was used in expelling water (free, emulsified and dissolved water) from the oil prior its use in the refrigerator. Water exists in oil in three phases (dissolved, free and emulsified) and one major equipment that is suitable for removing all of the three water forms, is the Filson Filters Vacuum dehydrator (the system can also remove gases and particulate matter entrained in oil). It comprises of three sections, a heating section, a distillation/vacuum section and a filtering section comprising of dual-stage filters. The Copeland 46B oil was first loaded onto the oil sump of the equipment, the equipment was then turned on and the temperature of the dehydrator was adjusted to 65 °C; this is so as to prevent oil from visbreaking/experiencing thermal breakdown since it is impossible to remove dissolved water from oil without the application of heat. As the temperature of the oil rose up to 65 °C, the distilled water was then collected into a distillation chamber/vacuum wherein is attached a vacuum pump which helped to create a vacuum by sucking and pumping out the expelled/recovered water at 18-27 mmHg. Water dispersion took place in the vacuum where dissolved water and gases in the Copeland 46B oil were boiled off in order to ensure effective oil-dehydration while still retaining the properties of the Copeland oil. The dehydrated water was then conveyed via the discharge section of the pump to the filter where particulate matter was removed. At this point, the heat supplied to the unit was lowered until the oil became cool. Thereafter, the dehydrated oil was then drained out from the oil sump of the dehydrator for use in the refrigerator. Afterwards, several 500 mL portions of the dehydrated Copeland oil were then made available for mixing with the CuNP and SiNPs.

Synthesis of the nanolubricating oils. In preparing the 0.5 M CuNP and Copeland 46B oil mixture, 0.5 M CuNPs were mixed with 500 mL Copeland 46B oil and sonicated separately at 40, 80 and 120 kHz respectively for 1 min each. The same procedure was repeated in preparing the 1 M CuNPs and Copeland 46B mixture, 1.5 M CuNPs and Copeland 46B mixture, 0.56 M SiNPs and Copeland 46B mixture, 1.29 M SiNPs and Copeland 46B mixture and, 1.69 M SiNPs and Copeland 46B mixture respectively.

Distinctive and respective molarities of 0.5–1.5 and 0.56–1.69 mol/ dm<sup>3</sup> of copper and silicon nano-compressor oils were made by means of the ultrasonic transducer which helped to enable uniform mixing of the nanoparticles with the Copeland 46B/compressor oil before they were poured into the oil-drum of the compressor; an equal mass in each case, i.e., 1.5 g each of CuNPs or SiNPs was weighed and mixed separately with the lubricating oil, this system was tested against the pristine Copeland 46B oil as well as the hybrid nano-entrained oil system containing equal portions (0.75 g each of CuNPs and SiNPs). The oils were then sonicated at varying frequencies ranging from 40 to 120 kHz.

# Estimation of essential parameters during sonication and COP of the refrigerator running on nanocompressor oils

(i) Determination of Essential Sonicatior Parameters.

A sonicator bath was set up with the different nanofluids placed in the bath. Thereafter, the equipment was connected to its power source. The frequency of sonication/number of oscillations/vibrations per unit time which defines the difference between the spatial and angular frequencies was set at a specific value say 40, 80 and 120 kHz; the period of oscillation or time (T) taken to complete a cycle/loop was determined using (1).

$$T = \frac{1}{f} \tag{1}$$

f = Frequency, measured in Hz, T = Period, measured in seconds.

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The power or heat transfer rate in Watts or J/s, also known as the

sonication-energy transferred/expended per unit time from the sonicator to the mixture of the nanoparticles and the Copeland 46B oil was determined using (2ä):

$$Power = \frac{workdone}{time} = \frac{Energy}{time}$$
(2a)

Since work = PV, while Power = PV/t or PQ where Q = volumetric flow rate (V/t) of fluid (at resonance, the frequency of vibration of the sonicator fluid/water = that of the oil mixed with nanoparticles). Since P =  $\rho$ hg, where  $\rho$ , h and g are the density of fluid, height of fluid and acceleration due to gravity respectively. Therefore,

Power =  $\rho$ hgQ; then from (2a), Energy = power\*time i.e.,  $\rho$ hgQ\*sonication time (2b).

Since the heat lost by the sonicator probe/bath = the heat gained by water, the representative equation is then given by (3).

$$H = mc_p \theta \tag{3}$$

H = change in enthalpy, m = mass of water,  $C_p$  = specific heat capacity of water and  $\theta$  = change in temperature of water.

Note: The specific heat capacity of water is constant (i.e., 4200 kJ/kg.K), while the change in water temperature was determined by measuring the initial temperature of water at ambient conditions and subtracting the value from the final temperature of water after sonication at the desired frequency.

(ii) Charging the 50-L LG refrigerator with refrigerant (250 g of R134a).

The type of refrigerant was first identified by carefully looking at the back of the LG refrigerator; a screw driver was used to open up the screws. The compressor nameplate on the compressor which is located behind the refrigerator was then looked at in order to identify the apt refrigerant that it can be recharged with as specified by the manufacturer (this can also be found on the compressor cover/lid/hatch cover). The refrigerant was weighed to ascertain its weight (i.e., 250 g). The refrigerant line was then blocked/closed by shutting the saddle valve that is installed on the copper capillary tube/pipe, positioned between the compressor and the evaporator. With the help of the hexagonal head screw, the valve was held in place, while the hexagonal head wrench was employed in tightening the screws on the valve. With the help of a refrigerant value adapter installed on the saddle value which makes for the safety of the refrigerator, the valve and service port of the refrigerator were secured. By means of a hose which was connected to the R134a cylinder, the hose which is usually housed in a kit containing a colourful meter gauge alongside a thread for connecting the refrigerant cylinder and service port was connected via the adapter already connected to the saddle valve. This was achieved by connecting the other end of the hose to the adapter by means of the hexagonal-head wrench which was used to adjust the screw. The refrigerator was then turned on at this point and allowed to run for about 5 min until a stable pressure (i. e., no pressure drop) was attained on the colourful meter gauge. Next, the refrigerant cylinder port was then opened so as to convey the refrigerant from the cylinder into the refrigerator; while charging in the refrigerant, the service port was closed at one minute interval to check the inherent pressure until the specified pressure of 25 psi was attained/ read-off from the pressure gauge meter. At this point, the saddling valve was then shut using the hexagonal-head wrench while the hose was disconnected from both ends to which it was connected during the refrigerant-charge process. The compressor lid was then replaced in its proper position, and held in place with the screws.

(iii) Charging the Copeland 46B Oil into the Compressor of the LG-refrigerator.

Lack of oil in a compressor can lead to compressor damage or malfunction. The presence of oil in the compressor makes for efficient lubrication while also keeping the compressor cool and in good working condition, thus minimizing wear and tear caused by friction of the moving parts. Personal Protective Equipment such as coverall, safety googles, safety boots and gloves were worn in the course of carrying out the experiment. The tools used in recharging the compressor with the Copeland 46B oil include an open head wrench, ratchet wrench and a double gauge manifold set. With the help of the wrench, the stem cover to the suction service valve was removed. The ratchet wrench was then used in shutting the compressor's suction service valve by adjusting its stem to the front seat. Using a double gauge manifold set, the vacuum pressure was monitored and noted. Thereafter, the oil drum was then connected to the suction/charging line of the compressor; the drum was positioned in an upside-down manner so as to ensure easy flow of oil into the compressor. Next, the saddle valve on the compressor was opened so as to allow the flow of the Copeland 46B oil through the inlet/suction side of the compressor. While observing the oil gauge level indicator on the compressor, the saddle valve was shut as soon as the oil level attained the full charge mark. The valve/control knob on the Copeland 46B oil drum was also closed. The suction service valve was then opened with its stem moved to its initial/back seat position. At this point, the suction, discharge and oil pressure were compared with the recommended standard values as stated in the LG-manual. The stem cover of the suction service valve was then closed and routine checks were then made in order to ensure there was no oil leakage except for the little spills experienced while charging the Copeland 46B oil; these spills were thoroughly wiped out from the body of the compressor with a dry cotton cloth at the end of the oil-charging process. At the end of the process, since the refrigerant is expected to mix with the pristine Copeland 46B oil, the refrigerator was degassed by emptying the residual R134a into an empty cylinder and the pristine Copeland oil was drained from the compressor into an empty container prior the start of the next operation, in which the compressor was recharged with 0.5 M CuNP-Copeland oil as well as 250 g of R134a. At the end of the operation, the refrigerator was recharged with R134a and the different nano-Copeland oils (i.e., the 1 M, 1.5 M and 0.56 M, 1.29 M and 1.69 M CuNP and SiNP-oils) respectively by following the procedure discussed above.

Note: The procedures discussed in sections "Estimation of Essential Parameters during Sonication and COP of the Refrigerator Running on Nanocompressor Oils ii-iii" were repeated for each of the synthetic oils prepared in section "Dehydration and Synthesis of Nanolubricating Compressor Oils ii".

(iv) Determination of COP of Refrigerator.

A household refrigerator of 50 L capacity was initially charged with refrigerant (R134a) and pristine Copeland 46B oil and commissioned in order to establish the effect of sonication speed/frequency, nanoparticle concentration, pH, pull down time and thermal conductivity of the different fluids on the performance of the compressor. Temperaturemeasurements (T1, T2, T3, T4 and T5 compressor inlet, compressor outlet, condenser outlet, throttle pipe outlet and Evaporator respectively) at different points were taken using type-k thermocouples and the thermocouple probes were made to have good contacts with those parts. Another thermocouple whose probe was extended to the internal chamber of the refrigerator was also connected to the refrigerator to read off the inherent temperature inside the refrigerator; this was done by creating a bore where the probe of the thermocouple was passed and the edges of the bore were sealed with ceramic dust plastered on the surface to prevent heat loss to the environment. It takes the refrigerator running on R134a and pristine Copeland oil 3-4 h to shut off and go into its defrost cycle, whereas, for the doped oil, it takes the refrigerator about 4-6 h to shutoff prior going into its defrost cycle owing to the modification of the properties of the oil, hence, tripping off is only evident or intermediate at 30 min interval within the experimental phase within which the readings were taken and the system's compressor only shuts/cuts off completely as soon as the set temperature of the sensor is reached. It should be noted that the introduction of nanoparticles into the Copeland oil helped to modify as well as influence the steady state temperature or properties of the compressor-oil. Also, the camera temperature sensor (a knob that can be turned clockwise and anticlockwise), was used to adjust the temperature-setting of the

refrigerator to 10 °F (i.e., about -12.2 °C) owing to the level of cooling anticipated and since the lowest temperature attained by the refrigerator at the pull down time was -11 °C, the refrigerator did not experience any trip off during the investigation since the set temperature was not attained.

In this research, R134a, a HFC was employed as refrigerant owing to its wide availability, high thermal stability, high viscosity index and its high measure of compatibility with synthetic oils such as Copeland 46B/ polyol ester (POE)/polyalkelyneglycol over its competitive counterparts such as alkylbenzenes which are more suitable for HCFCs or CFC refrigerants. The filter dryer of the unit is compatible with a filter dryer of molecular sieve 3-Angstrom whose humidity absorption capacity is compatible with oil systems whose humidity is <20 ppm, with moderate internal volume and refrigerant charge as recommended by the manufacturers (LG) [64].

From reports, R134a only has zero ODP but its global warming potential is approximately 1430 for a 100-year span using CO<sub>2</sub> as reference gas, which is still higher compared to that of hydrofluoro-olefins (HFOs) and hydrocarbon refrigerants (HCs). However, R134a is still in use in some countries as the major refrigerant in refrigerators; this is because, in this new wave of nanolubricant application in compressors used in refrigerators, the incursion of nanoparticles helps to ensure the high miscibility of synthetic/mineral oils used in compressors alongside the energy saving capacity of the unit which indirectly implies reduced emissions; hence, the need to search for viable approaches to lower the GWP of the commonly available refrigerants and since the phasing out of the very commonly used refrigerants implies higher costs of their competitors, the use of nanoparticle entrained compressor oils have proven to be somewhat useful in this guise. Also, another very helpful tip in using R134a is ensuring that there is no leakage of any sort when it is in use; this will also help limit the emissions resulting from its use during refrigeration; other advantages include its low flammability compared to hydrocarbon refrigerants such as (R600a and R290) as well as other new generation refrigerants, high vapour density of 4.17 kg/m<sup>3</sup> (at 101.3 kPa), high critical temperature (101.06 °C) and critical pressure (4059.3 kPa) over its several existing competitors. In addition, the approved Embraco substitute refrigerants for R134a are R513A and R513A as alternative refrigerants for Embraco R134a compressor within low boiling point (LBP) and high boiling point (HBP) applications, thus maintaining same operating envelope as with R134a refrigerant within other Embraco application guidelines; in addition, CFCs are chlorofluorocarbons containing chlorine and chlorine is one component that must be avoided according to compatibility data obtained from refrigerant suppliers of HFCs such as R600a, R290 and R134a. Substances containing chlorine and silicone are not usually recommended for systems that use such refrigerants going by the manufacturer's specification.

An integrated service port was provided on the refrigerator for charging/recovering the spent refrigerant. The test rig established in this study is similar to that established by Damola et al. [65]. The different tests were done for a duration of 240 mins per run for the pristine Copeland oil and the nano-particulate oils. The amount of refrigerant charged into the EM series Embraco compressor is 250 g of R134a which is according to the manufacturer's specification. The COP of the refrigerator was then determined by taking the temperature readings from the thermocouples (T1, T2 and T3) and matching those values with a standard enthalpy chart (see reference table A.6- Standard enthalpy-entropy data for vapour compression systems at different temperatures and pressures-Appendix section of Supplementary File); from Table A.6, the enthalpy values h1-h3 were obtained by matching temperatures to corresponding enthalpies: saturated vapour enthalpy (h1), superheated vapour enthalpy (h2) and immersed liquid enthalpy (h3) as given in (4).

$$COP = \frac{h1 - h3}{h2 - h1}$$
(4)

Fig. 3a-c (excerpt from Sanni et al. [17]) and d, show the schematic



**Fig. 3.** Refrigerator cross-sections showing a. condenser cross sectional dimensions of the refrigerator, b. K-type thermocouples T1-T5 (from left to right) and the thermocouple T6 placed ontop of the refrigerator c. refrigerator-cross section comprising of the evaporator, condenser, throttle valve/flow meter and compressor. Adopted from Damola et al. [65] and Sanni et al. [17] (all dimensions are in mm; 1 mm on paper represents 5 mm on the equipment), B. vapour compression cycle indicating the positions of the thermocouples attached to the external section precisely the back section of refrigerator (a last thermocouple T6 whose probe is passed through a bore created in the central part of the refrigerator; the edges of the bore are sealed all round so as to help prevent leakages or temperature loss from the internal section of the refrigerator).



# (d)

Fig. 3. (continued).

sections of the refrigerator and thermocouples used in taking temperature readings at the experimental phase.

Note: Considering each oil and the charged refrigerant R134a, the experiments and procedures were repeated thrice and the average values read off from the five thermocouples (T1-T4 and the one inserted into the cooling chamber) were taken at the end of the experiment.

#### Uncertainty procedure analysis

The uncertainty analysis procedure adopted in this research is that in which the experimental result "r' was computed using a data reduction equation alongside the basic measurements of values of component"j" as presented in (5); this simulates the procedure adopted by Colman and Steel [66].

$$r = r(X_1, X_2, \dots, X_j)$$
 (5)

 $X_1, X_2, ..., X_j$  are the set of input variables while r is the output. In this work, the uncertainty of the experimental results was computed as a first order-type using the root-sum-square of the product of the uncertainties

of the measured variables and the sensitivities of the results to the inherent changes in such variables as presented in (6).

$$U_r = \left(\frac{\partial r}{\partial X_1}U_{X1}\right) + \left(\frac{\partial r}{\partial X_2}U_{X2}\right) + \dots + \left(\frac{\partial r}{\partial X_j}U_j\right)^2$$
(6)

 $U_{XI}$ ,  $U_{X2}$ .... $U_{Xj}$  are the associated uncertainties with respect to the measured variables while the corresponding partial derivatives are the sensitivity coefficients associated with each variable under consideration. In the experimental uncertainty analysis, a set of data/fluid properties (density, viscosity, pH, thermal conductivity, etc.) were used in the computational analysis to compute the results from which decisions were informed; the computed results were found to be analogous to the experimental results. Also, the sensitivities of the calculated performance parameters to small changes in each of the input parameters were determined using the estimated sensitivity coefficients. Hence, equation (6) may be rewritten as (7):

$$\left(\frac{U_r}{r}\right)^2 = \left(\frac{X_1}{r}\frac{\partial r}{\partial X_1}\right)^2 \left(\frac{U_{X1}}{X_1}\right)^2 + \left(\frac{X_2}{r}\frac{\partial r}{\partial X_2}\right)^2 \left(\frac{U_{X2}}{X_2}\right)^2 + \dots + \left(\frac{X_j}{r}\frac{\partial r}{\partial X_j}\right)^2 \left(\frac{U_{Xj}}{X_j}\right)^2$$
(7)

 $\left(\frac{X_1}{r}\frac{\partial r}{\partial X_1}\right)^2$ ,  $\left(\frac{X_2}{r}\frac{\partial r}{\partial X_2}\right)^2$  and  $\left(\frac{X_1}{r}\frac{\partial r}{\partial X_1}\right)^2$  are the normalized sensitivity coefficients which help to amplify, diminish/propagate the unchanged individual normalized uncertainty values  $\left(\frac{U_{X1}}{X_1}\right)^2$ ,  $\left(\frac{U_{X2}}{X_2}\right)^2$  and  $\left(\frac{U_{X1}}{X_1}\right)^2$  so as to effect the uncertainties in the result. The normalized sensitivity coefficients, help to identify the uncertainties associated with the input parameters to which the performance parameters are most sensitive regardless of the levels of accuracy of the specified input parameters. However, the sensitivity coefficients only reveal a small fraction of the whole piece, hence, they must be combined with the actual uncertainty estimates to give the uncertainty contributions of each experimental input parameter. The relative contribution of each input parameter is the square of the sensitivity coefficient's uncertainty value, normalized by the square of the uncertainty in the performance parameter. This is expressed as:

$$R_c = \left(\frac{\frac{\partial r}{\partial X_i} U_{X_i}}{u_r^2}\right)^2 \tag{8}$$

As soon as the uncertainties in the input parameters were specified, the relative contribution ( $R_c$ ) helped to identify the dominant uncertainty contributors as listed in Table 1.

Table 1 comprises of the measured uncertainties associated with each variable measured during experimentation.

#### **Results and discussion**

From the results shown in Fig. 4, upon adding 1.5 g each of the silicon and copper nanoparticles (SiNPs and CuNPs) to the oils, there was a reduction in the density of the unsonicated Copeland 46B compressor oil with the copper doped compressor oil having the least density, i.e., the CuNPs gave a stronger density-reduction on the blank compressor oil relative to those of the silicon-doped and blank Copeland oils with corresponding densities of 758.35, 782.5 and 791.28 kg/m<sup>3</sup>; these results are in accordance with those obtained by Sanni et al. [17]. The change in the density of the oil is due to the relative reactivities of the metals; copper is more reactive than silicon and hence causes a loss in mass which translates to lower density losses for the unsonicated oils since they were not stirred relative to those presented in Fig. 5.

To determine the effect of sonication on the oils, the three oils presented in Fig. 4 were sonicated at 40 kHz. Fig. 5 shows corresponding

# Table 1

Uncertainties associated with the measured variables.

Instrument	Parameter measured	Unit	Uncertainty
Pressure	Pressure gauge	bar	$\pm 0.01$
Temperature	K-type thermocouple	°C	$\pm 0.01$
Thermal	Conductivity meter	W/	$\pm 1$
conductivity		m.K	
Density	Anton Paar density meter	kg/	$\pm 0.005$
-	-	m <sup>3</sup>	
Viscosity	Viscometer (Herzog Viscometer	cP	$\pm 0.01$
-	HVM 472 HVM01		
Yield stress	Marlven Panalytical Kinexus Pro +	kg/	$\pm 0.1$ %
	Rotational Rheometer	m <sup>2</sup>	
pН	Hanna 211 pH meter	_	$\pm 0.01$
Absorbance	U-V spectrophotometer- 7310 visible	_	$\pm 0.005$
	Scanning Spectrophotometer		
Time	Stop watch	s	$\pm 0.1$
Mass	Weighing balance (Stwart systems Pro)	g	$\pm 0.05$
Lubricity	OFITE Lubricity	-	$\pm 0.001$
coefficient	tester		

increases in the densities of the sonicated oils relative to those of the unsonicated oils at increased sonication time and frequency for each of the oils. The densities of the oils were found to be 768.48, 790 and 793.5 kg/m<sup>3</sup> for the CuNP-doped, SiNP-doped and the blank sonicated compressor oils, respectively. The incursion of the Cu and SiNPs into the copeland oil by sonication makes the lubricant lighter as a result of the reactivities of the nano-metals which in turn lower the viscosities of the nanolubricants for ease of lubrication of the compressor parts.

#### Absorbance and transmittance

Under UV light, the SiNP-Coppeland 46B, CuNP-Copeland 46B and the blank Copeland 46B oils were seen to absorb light at different wavelengths and the results are as shown in Table 2. The nanoparticleentrained compressor oils absorbed higher light intensities more than the blank Copeland 46B oil. Thus, in order of increasing absorbance, the results are Copeland 46B < SiNP-Copeland 46B < CuNP-Copeland 46B oils; the reverse order, is the order of increased transmittance since absorbance is inversely proportional to transmittance i.e., Abs  $\alpha$  1/T. T = I/Io, where Io is the intensity of light which strikes the sample and I is the intensity of light received after light rays went through the sample. Again, among the three oils, the CuNP-oil gave the highest absorbance because, the CuNP absorbed more light compared to the SiNP owing to the latter's ability to project its shiny luster when in contact with light.

## pH of reagents and Copeland oil

The Hanna pH 211 m was used to determine the pHs of the fluids. The equipment was first calibrated according to the manufacturer's instructions using the pH buffer 7 and deionized water as the calibration fluid. Thereafter, the electrode/pH-probe was then inserted in the samples. The values were taken in three runs so as to ensure high accuracy in the data obtained. Table 3 shows a decrease in pH at lower concentrations of NaOH with the measured pHs of the reagents used in carrying out this research.

Table 4 shows the effect of adding ascorbic acid to the copper precursor/CuSO<sub>4</sub>·5H<sub>2</sub>O solution. The results show a spike in pH from 1.1 to 2.35 (drop in acidic strength) for the 0–5–1.0 M Copper sulphate pentahydrate solution, after which it dropped at higher concentrations of the pentahydrate solution i.e., 0.5–1.5 M; this then suggests an optimum pH at a concentration of about 1.0 M CuNP, beyond which the solution's acidic strength begins to rise again; the findings conform with the suggestion in ref [40] which stipulates an optimum nanoparticleconcentration for best performance of refrigeration systems. Also, it was observed that increasing the concentration of ascorbic acid for a constant mass of CuSO<sub>4</sub>·5H<sub>2</sub>O increased the resultant pH of solution.

In order to establish the effect of temperature on the density of the non-sonicated nanoparticle-Copeland oils, the non-sonicated 0.5–1.5 M nano-doped copper and silcon-doped compressor oils, containing 1.5 g each of SiNPs and CuNP, were subjected to different temperatures. The results are as shown in Figs. 6 and 7, respectively. Changes in temperature from 0 to 60 °C, had more effect on the densities of the SiNP-Copeland oil, where the recorded densities for the 0.56, 1.29 and 1.65 M SiNP-Copeland oil were in the range of 0.81–0.89, 0.81–0.9 and 0.84–0.9 kg/m<sup>3</sup> respectively, while for the 0, 1.0 and 1.5 M CuNP-Copeland oils, the corresponding densities are 0.862–0.91, 0.895–0.91 and 0.912–0.94 respectively (Fig. 7). Thus, from the results, the CuNPs were more thermally stable relative to the SiNPs; these results are in agreement with those of ref. [40]. This is because, based on the periodicity of elements, copper whose molecular weight is 63.5 g/mol is denser than silicon whose molecular weight is 28.1 g/mol.

The pH of the pristine Copeland oil was determined and recorded. Thereafter, the pH measurements were taken when 1.5 g of each nanoparticle was sonicated with 500 mL of the Copeland oil; their corresponding pHs were found to be 5.8, 6.2 and 8.3 for the pristine Copeland, CuNP-and the SiNP- oils respectively (Fig. 8). Sonication



Fig. 4. Density tests for the blank and unsonicated nanofluids.



Fig. 5. Density of the blank and nanocompressor oils sonicated at 40 KHz.

Table 2		
Absorbance of t	he different	Fluids.

Compressor Oil	Wavelength #1 (190 nm) A1	Wavelength #2 (1100 nm) A2	Difference in Absorbance at both extreme ends (A1-A2)	Ratio A1/A2
Copeland 46B	1.571 (2.7) <sup>a</sup>	1.679 (2.1) <sup>b</sup>	-0.108 (0.6) <sup>c</sup>	0.936 (1.292) <sup>d</sup>
Si- Copeland 46B	1.611 (1.4) <sup>a</sup>	1.771 (1.7) <sup>b</sup>	-0.160 (0.3) <sup>c</sup>	0.901 (1.178) <sup>d</sup>
Cu- Copeland 46B	1.871 (1.3) <sup>a</sup>	1.959 (1.1) <sup>b</sup>	-0.088 (0.2) <sup>c</sup>	0.955 (0.823) <sup>d</sup>

\*Values outside the brackets are absorbance values at different wavelengths: 190 nm, 1100 nm, difference in absorbance values and ratios, while those enclosed in brackets (), are their corresponding transmittances: <sup>a</sup> is transmittance at 190 nm, <sup>b</sup> is transmittance at 1100 nm, <sup>c</sup> is the difference in transmittance at 190 nm while <sup>d</sup> is the ratio of absorbances at both extremes.

induced some measure of temperature increase in each of the nanoentrained oils owing to the intense heat provided by the sonicator bath at constant frequency and sonication time. There was a decrease in acidic strength of the oil owing to the fact that both metals are basic in nature. However, the SiNPs had stronger reduction effect on the acidic strength of the Copeland oil, thus stretching the pH of the mixture to the weakly alkaline region, although that of the CuNP-entrained oil was seen to be weaker in acidic strength than the pristine Copeland oil. This goes further to stress that the corrosivity of the sonicated nano-lubricant containing the Cu and SiNPs was reduced or lowered as a result of the presence of the SiNPs; ultimately, this also helps to improve the service life of the compressor.

#### Electrical and thermal conductivity

Electrical conductivity is a diagnostic property which expresses how easily, electrical charges flow through a given material when under the

# Table 3pHs of NaOH solution at varying concentrations.

NaOH (M)	pН	Reagents/Oil	pH value
1	13.83	Copper sulphate pentahydrate (CuSO <sub>4</sub> ·5H <sub>2</sub> O)	4.33
0.8	13.76	Ascorbic acid (C <sub>6</sub> H <sub>8</sub> O <sub>6</sub> )	3.28
0.6	13.65	NaBH <sub>4</sub>	7.40
0.4	13.54	Oleic acid	9.53
0.2	13.46	Copeland oil	5.80

#### Table 4

pHs of Copper Nanoparticles at Different Concentrations.

Copper pentahydrate solutions	pH after 20 min of reaction with acid	pH at the end of reaction with ascorbic acid
0.5	1.1	0.956
1.0	2.35	1.455
1.5	1.5	1.32

influence of an electric field. The electrical conductivity of the blank non-sonicated compressor oil was compared with those of the 1.5 gdoped 0.5–1.5 M concentrations of non-sonicated CuNP and SiNP- oils (500 mL) in terms of their responses to thermal electical pulses/molecular darts and it was discovered that the conductivity of the CuNP-oil was highest (Fig. 9a); this is not farfetched, because copper is a better conductor relative to silicon. However, the conductivity of silicon was higher than that of the pristine Copeland oil. High conductivities of copper and silicon nanoparticles increased the thermal conductivities of the blank compressor oil with copper increasing the conductivity of the compressor oil better than silicon. Since the oil with the highest conductivity was the copper-doped Copeland oil, this oil was chosen to determine the effect of changes in sonication speed/frequency (from 40 to 80 kHz) on the oil's conductivity; Fig. 9b shows that the sonicated



Fig. 6. Densities of nonsonicated SiNP-Copeland oil at different temperatures.



Fig. 7. Densities of nonsonicated CuNP-Copeland oil at different temperatures.



Fig. 8. pH of the Copeland and nano-doped oils.

CuNP-oils conductivity increased with sonication speed.

According to Fig. 9b, the thermal conductivity of the nanolubricant containing the Cu and SiNPs increased with frequency because, the variation of polarization with frequency of vibration at the electrode interface of the sonicator controls the alternating current (AC) flowing from it; these findings are in accordance with those of Wang and

Mujumdar [67], Saidur et al. [25], Kamyar et al. [3] and Pirahmadian and Ebrahimi [68]. Thus, at increased frequencies, the fluid's conductivity increased due to the release of free/mobile space-charges. According to Jiang et al. [40], the thermal conductivity, viscosity, density and specific heat of a system comprising of nano-CuO/R-134a, increased with increased particle concentration/vol%, whereas, the properties



Fig. 9. Thermal conductivity of the non-sonicated oils, b. Influence of sonication frequency and the conductivity of the Cu-Copeland 46B oil.

decreased with temperature, thus suggesting an optimal particle volume fraction for improved performance.; these observations are in agreement with the findings of this study.

#### Rheological properties of the nanofluids

#### Plastic viscosity

Viscosity is a measure of oil's resistance to flow. It decreases with an increase in temperature and increases with decrease in temperature as a result of an increase in the cohesive forces between the molecules present in the liquids.

The plastic viscosities of the oils were seen not to be altered prior sonication thus giving a constant plastic viscosity (19 cp) for each fluid (Fig. 10a). However, upon sonicating 1.5 g in 500 mL of the nano-doped oils, there were significant variations in the plastic viscosities of the fluids caused by the effects of heat generation and cavitation within the oils. In Fig. 10b, the plastic viscosities of the pristine Copeland, CuNP-Copeland and SiNP-Copeland oils dropped to 18, 16 and 14 cp

respectively thus confirming the effect of sonication on the plastic behaviours of the oils within 1 min of sonication time since the equipment could not go longer than 1 min within a resting time/lag phase of about 30 min. This further implies that the presence of nanoparticles in the oil gave rise to lower plastic viscosities which in turn reduced/slowed down the wave velocity imposed on the fluid, thus lowering its wave frequency. In order to examine/understand the effect of frequencyvariation on the plastic viscosities of the nano-doped oils, the CuNPcopeland oil was adopted for this test since it gave higher plastic viscosity relative to the SiNP-Copeland oil. From Fig. 10b, the sonicated CuNP-oil (comprising of 1.5 g CuNPs in 500 mL) at 40 kHz gave the lowest viscosity and it can be confirmed that the plastic viscosity of the CuNP-oil increased with sonication speed with the result at 120 kHz being the highest plastic viscosity; the corresponding plastic viscosities of the 40, 80 and 120 kHz sonicated oils are 19, 20 and 22 cp respectively. Fig. 11 also shows the respectve plastic viscosities increasing with sonication speed for the 1 M CuNP-oil.



Fig. 10. a. Plastic viscosities of the nano-doped oils before sonication, b. Plastic viscosity of nano-doped oils after sonication.



Fig. 11. Plastic viscosities of the 1 M CuNP-oil at different sonication frequencies (effect of frequency on plastic viscosity).

#### Apparent viscosity

Apparent viscosity  $(\boldsymbol{\eta})$  is the proportion of shear stress applied to a liquid to the shear rate.

Based on the results obtained in Fig. 12a prior sonication, the apparent viscosities of the oils were, 20.5, 20 and 19.5 cp for the Copeland, CuNP- and SiNP- oils respectively. The measurements taken at sonication frequency of 40 kHz and sonication time of 60 s, for each fluid containing 1.5 g each of 1.0 M and 0.56 M CuNP and SiNP respective concentrations of each nanoparticle in 500 mL of the Copeland oil, are presented in Fig. 12b; the apparent viscosities of the fluids were seen to be in the following decreasing order of magnitude for the oils: Pristine Copeland < CuNP-oil < SiNP-oil.

#### Yield stress

The yield stress of a compressor oil is indicative of the oil's elastic limit as well as the beginning of plastic behaviour in the oil; the measured yield stresses of the non-sonicated oils are in the following increasing order of magnitude: SiNP-oil ( $1.7 \text{ kg/m}^2$ ) < CuNP-oil ( $2 \text{ kg/m}^2$ ) < Copeland oil ( $3 \text{ kg/m}^2$ ) (Fig. 13a); these results are in agreement with the findings of Sanni et al. [17]; the same trend was observed for all the oils at different sonication speeds, although the yield stresses reduced, however, they were highest for the Copeland oil, while those of the CuNP-oil were higher than those of the SiNP-oil at 40–120 kH. This then informs that, the nanolubricant containing the CuNP and SiNPs had lower yield stresses as imposed by the nanoparticles relative to the yield

stress of the undoped/neat lubricant.

In the experiment that gave rise to the data from which Fig. 13ad were generated, the mass of the nanoparticles and volume of Copeland 46B remained the same throughout i.e., 1.5 g each of 1 M CuNP and 0.56 M SiNPs respectively. 1.0 M concentration was used and 500 mL of Copeland 46B, with 1.5 g of Cu-Copeland46B and 0.56 M Si-Copeland 46B respectively. Vibrations in the oils may alter certain physical properties in the oils. Due to the importance of the phenomenological reduction in yield stress of the nanofluids, a study of the effect of the imposed yield stress on the oils by the variation in the sonicator speed was then necessary. The yield stress of the Copeland 46B, CuNP and SiNP-oils were monitored prior sonication as control-cases/references. Thereafter, the yield stresses of each of the oils were then determined in terms of the measured impact/intensity of vibration imposed by the sonicator on the oils after sonication. The effect of frequency was determined by adjusting the knob on the sonicator bath to 40, 80 and 120 KHz respectively; the results are as shown in Fig. 13b-d for the Copeland 46B oil, the CuNP-oil as well as the SiNP-oil respectively. In all cases, the yield stresses of the oils decreased with corresponding increase in sonication speed; it was  $3 \text{ kg/m}^2$  for the non-sonicated Copeland oil (see Fig. 13a) whereas, it ranged from 1.6 to 1.3 at frequencies of 40-120 kHz respectively (Fig. 13b). For the non-sonicated CuNP-oil, the estimated yield stress was 2 kg/m<sup>2</sup> but ranged from 1.9-1.6 kg/m<sup>2</sup> after sonication with corresponding frequencies of 40-120 kHz respectively. Based on the results, it can be deduced that, the CuNP and SiNPs



Fig. 12. a. Apparent viscosity of the fluids before sonication., b. Apparent viscosity of fluids after sonication at 40 kHz.



Fig. 13. a. Yield point of all the oils before sonication, b. Yield point of the pristine Copeland oil at different frequencies (after sonication), c. Yield point of 1 M Cu-Copeland 46B at different frequencies, d. Yield point of 0.56 M Si-Copeland 46B at different frequencies.

1.2

1

0.8

0.6

0.4

0.2 0

SiNP-Oil

d

imposed reduced vield stresses on the compressor oil.

1

0.8

0.6

0.4

0.2

0

CuNP-Oil

c

For the case of the sonicated SiNP-oil, the yield stresses ranged from 1.8 to 1.5 with corresponding frequencies of 40-120 kHz respectively; it is also pertinent to note that for this case, there was a slight up-shoot in yield stress i.e., 1.8 kg/m<sup>2</sup> of the sonicated oil at 40 kHz over the maximum yield stress (1.7 kg/m<sup>2</sup>), which was obtained for the nonsonicated SiNP-oil; this was adjudged to have been caused by excessive agitations/vibrations induced by the sonicator on the oils. Furthermore, besides the case of the SiNP-oil sonicated at 40 kHz, a drop in the yield stress was seen to correspond to higher frequencies of sonication for other cases. Again, 1.5 g each of 1.0 M concentration of the CuNP and 0.56 M SiNP were dissolved in 500 mL of the Copeland oil for each test. In addition, it was observed that the yield stress of the CuNPoil sonicated at 40-120 KHz gave a higher yield stress than that of the sonicated SiNP-oil at same frequency range. Hence, sonication speeds can be said to have an inverse relationship with the yield stresses of the nano-oils.

Evaluation of refrigerator performance using different concentrations of nano lubricants at different frequencies

80 kHz

An evaluation of the influence of the nano-doped oils on the refrigerator performance is necessary in order to ascertain the conditions for optimum performance. This demonstrates the effect imposed by the use of nanolubricants sonicated at different frequencies in contrast to using the pristine Copeland 46B oil and R134a as refrigerant. The coefficient of performance and pull down time of the refrigerator using the R134a refrigerant and Copeland 46B oil were compared to those of the R134a used alongside the nanolubricant systems at different concentrations and frequencies.

Pull down time of the vapour compression system for 0.5 % mass of Cu/Sioil mixed with R134a sonicated at different frequencies.

In Fig. 14a-f, the variations in pull down temperature and time were established. Fig. 14a shows the pull down temperature variation with time (0-18000 s) for the: R134a-Copeland system oil whose pull down temperature varies from 10 to -4 °C, that of the non-sonicated Copeland oil mixed with 0.5 M CuNPs which varies from 11 to -7 °C, the Copeland oil mixed with 0.5 M CuNPs sonicated at 40 kHz with corresponding



Fig. 14. T vs t for the refrigerator running on R134a and: a. 0.5 M CuNP-oil, b. 1.0 M CuNP-oil, c. 1.5 M CuNP-oil, d. 0.56 M SiNP-oil, e. 1.29 M SiNP-oil, f. 1.69 M SiNP-oil \*R134a refers to the condition where the refrigerator uses the pristine Copeland and refrigerant as operating fluids for the vapour compression system.

temperatures ranging from 13 to -7 °C, the sonicated 0.5 M–CuNP oil at 80 kHz whose corresponding temperatures are in the range of 10 to -7 °C and the CuNP-Copeland oil sonicated at a speed of 120 kHz with upper and lower limit temperatures of 10 and -11 °C respectively. This then implies that, of all the oils considered in Fig. 14a, the 0.5 M Cunano-entrained oil gave the best cooling effect (-11 °C) at a pull down time of 18000 s; this is an improved result over the results obtained by Sanni et al. [17] for a system whose Copeland/compressor-oil was doped with 0.08 M silver and 1.6 M copper nanoparticles, however, there is an extension in pull down time to 18,000 secs as obtained in this study compared to 14,000 secs which was recorded in ref. [17] for the case of CuNP- and AgNP-oils.

In Fig. 14b, the upper and lower limit pull down temperatures at 0–18000 s for the R134a-Copeland system oil, spans from 8 to -4 °C. For the non-sonicated Copeland oil mixed with 1.0 M CuNPs, the temperature limits are 8 to -10 °C, while for the Copeland oil mixed with 1.0 M CuNP and sonicated at 40 kHz, the corresponding temperatures ranged from 10 to -11 °C. For the 1.0 M–Copeland oil at 80 kHz, the corresponding temperatures are in the range of 10 to -10 °C, whereas for the CuNP-Copeland oil sonicated at 120 kHz, the temperature varied from 8 to -11 °C. Thus, of all the oils considered in Fig. 14b, although sonicating the oils at 40, 80 and 120 kHz gave same/near similar cooling effect of -11 °C at a pull down time of 18000 s, however, maintaining the sonication speed at 120 kHz for the 1.0 M Cu-nano-entrained oil will be most suitable for the 1 M CuNP-Copeland oil system.

In Fig. 14c, the 1.5 M CuNP-Copeland oil sonicated at 40–80 kHz was compared with the properties of the non-sonicated pristine Copeland oil as well as those of the non-sonicated 1.5 M CuNP-oil, with R134a as refrigerant. For the different oils, the observed pull down temperatures are in the range of 10 to -4 °C for the R134a mixed with the Copeland oil system. The temperature ranged from 6 to -9 °C for the non-sonicated 1.5 M CuNP-oil sonicated at 40 kHz. However, the recorded temperature ranged from 6 to -10 °C for the 1.5 M CuNP-oil sonicated at 80 kHz which also corresponds to the lower and upper limit temperatures (i.e., 6 to -10 °C) for the 1.5 M CuNP-oil system sonicated at 120 kHz. In essence, the CuNPs used in the Copeland oil alongside the R134a helped to improve the COP which translated into enhanced cooling effect of the refrigerator amidst the stretched range of pull down time.

For the case of the silicon entrained oil systems, the results in Fig. 14d-f show the different variations in temperature and pull down time for the 0.56, 1.29 and 1.69 M SiNP-oil systems, respectively. In Fig. 14d, between 0 and 18000 s, the upper and lower limit temperatures are 8 and -7 respectively, for the R134a-0.56 M SiNP-oil system. For the R134a mixed with 0.56 M SiNP-oil sonicated at 40 kHz, the temperature spanned from 10 to -7 °C, it was in the range of 0 to -6 °C for the 0.56 M SiNP-oil sonicated at 80 kHz whereas, the lower and upper limit temperatures are -7 and 0 °C for the 0.56 M SiNP-oil sonicated at 120 kHz for a pull down time of 0-18000 s. In Fig. 14e, the R134a and pristine Copeland oil gave pull down temperatures in the range of 10 to -5 °C. The temperature spanned between 12 and -4 °C for the 1.29 M SiNP non-sonicated-oil, but was between 13 and -4 °C for the 1.29 M SiNP-oil sonicated at 40 kHz. The values ranged from 12 to -4 °C for the 1.29 M SiNP-Copeland oil sonicated at 80 kHz whereas, the corresponding upper and lower limit temperatures for the 1.29 M SiNP-oil sonicated at 120 kHz are 13 and -4 °C respectively.

Considering the results in Fig. 14f, for a pull down time of 0–18000 s, the R134a and pristine Copeland oil system gave upper and lower limit temperatures of 10 and -5 °C respectively, while for the other cases where the system was operating on R134a and unsonicated 1.69 M SiNP-oil only, 1.69 M SiNP-oil sonicated at 40 kHz, 1.69 M SiNP-oil sonicated at 80 kHz and 1.69 M SiNP-oil sonicated at 120 kHz, the corresponding range of temperatures are 10 to -4 °C, 10 to -4 °C, 11 to -4 °C and 11 to -4 °C respectively. Comparing the results for all the SiNP-Copeland oil systems, it is clear that using SiNP-particle concentration of 0.56 M mixed with the Copeland oil sonicated at 120 kHz gave the best cooling

effect (i.e., -7 °C), whereas, based on both nano-oil systems, the 1 M CuNP-Copeland oil system gave the best optimized cooling effect (-11 °C) at a speed of 120 kHz owing to the improved lubrication effect induced on the compressor. Since the 0.56 M SiNP and 1 M CuNPs gave the best results, they were then combined to determine their synergistic influence on the refrigerator performance. Here, a frequency of 80 kHz was adopted. The results show that for the hybrid system (i.e., R134a and SiNP-CuNP-Copeland oil system), the refrigerant used with the combined non-sonicated SiNP and CuNP oil system gave temperature limits of 11 and -4 °C whereas, for the hybrid system sonicated at 80 kHz, the temperature limits spanned from 9 to -9 °C, this is suggestive of a reliable cooling effect (Fig. 15). Each run was performed separately for each oil for every 20 min, which is less than the average time for one complete cycle (30 min), for which the compressor tweaks off and delays a bit, before coming on-stream again. However, for each run, the R134a and the neat oil (i.e., R134a and pristine Copeland oil) were used and readings were taken at 20 mins interval with consideration given to the time-off and on of the compressor. At time off, the reading was stopped whereas, as soon as the compressor came on-stream, the taking of readings resumed for the next 20 mins until the final duration where steady state was attained such that there was no variation in temperature despite the time-extension. The ideal time spread could have been 3-4 h, however, with such modification on the properties of the fluid, the readings were allowed for up to 5 h to clearly ascertain steady state condition. Also, each reading was taken for about 240 min. Thus, looking at the graph in Fig. 15 for instance, steady state was actually attained in 4 h (14,400 s) where the lowest temperature recorded for the ordinary/pristine Copeland 46B oil used with R134a gave the lowest temperature of -4 °C, even at longer times up to 18,000 s. However, comparing this system with the hybrid oil comprising of 0.56 SiNP and 1 M CuNP oil used with R134a, steady state condition was altered by the nano-doped oil, hence, steady state was attained at 15,600 s down to the 18,000 s with a corresponding temperature of -9 °C; again, the reason for allowing the time stretch further/up to 18,000 s, is so as to fully confirm steady state condition beyond a point. Hence, in actual sense, steady state was attained at 4.33 h (15,600 s). Again, this is one mystery behind the use of the SiNP and CuNP-doped compressor oils. They have the ability to alter the properties of compressor oils such that the actual steady state condition is regulated owing to a stretch in the lowest attainable temperature. Well, without dopants, the refrigerator will attain its lowest temperature of - 4 °C within 4 h. Now, concerning Fig. 14a-f, each case was run separately but, in order to ensure high reproducibility, each experiment was run in triplicates (i.e., 3 experiments per run, so as to ensure high accuracy during data documentation; a minimum of 2 sets of concordant data were approved in the case where there was a slight variation in one of three readings). Again, in order to allow for close comparison, the different data generated were plotted on the same graph. In engineering, steady state condition is usually validated by a flat line indicating no changes in a parameter e.g., temperature with time.

Ideally, for some small refrigeration units/vapour compression systems/equipment, the compressor starts and shuts down frequently/ intermittently. At shut-down, the condenser-pressure and that inherent in the evaporator are equal owing to the flow of refrigerant (in this case R134a) from the condenser to evaporator. As soon as the compressor starts or picks up again, no doubt, there is usually a drag/time-lag in attaining the operating pressure required in the condenser and evaporator. Since the flow of refrigerant requires a higher input-power when the compressor is in the off position/restart state for a small refrigerating unit with capillary tubes, it then becomes somewhat necessary to understand the on-off operating characteristics of the system. An investigation was conducted to determine the on-off characteristics and effects of a compressor by taking temperature and pressure measurements on either side of the condenser and evaporator (heat exchanger) when the compressor is in on-off operating mode; the input-power at compressor start-up was also considered. The effect of refrigerant-flow on pressure,



Fig. 15. Pull down time vs temperature for the nonsonicated pristine Copeland oil and hybrid sonicated oil system @ 80 kHz.

temperature and power input were studied when the compressor was in off-mode. The important factors affecting energy conversion were also analyzed and the results showed that the prevention of the flow of refrigerant when the compressor is in off-mode can reduce the power input by about 4 % and the peak value of the input power by about 9.4 %. According to John and Yezhen [69], the cooling capacity can be increased such that the evaporating temperature and pressure approach steady state earlier. They developed a mathematical model for the compressor of a mini-sized refrigerator operating in off-mode and discovered that the exergy losses resulting from the flow of refrigerant during off operation as calculated, was found to be the minimum energy to be saved via preventing the refrigerant from flowing.

Two cases were considered where, case 1 involved conventional cycle measurements with refrigerant flowing through the capillary tube after compressor shut-down while case 2, involved cutting off the magnetic valve as soon as the compressor was shut-down, this in turn abated the flow of refrigerant out of the condenser. Bypass valves in series located between the compressor suction and discharge manifolds were seen to open rapidly during the compressor start-up stage in order to avoid the incidence of excessive torque.

The measurements lasted about a few minutes (i.e., 7 min) within the on and off cycles. The respective temperatures at the outer part of the condenser and evaporator were 35 and 18 °C. At this stage, the mixing of refrigerant in the compressor and evaporator stopped and it was observed that the inlet and outlet temperatures of the condenser and evaporator varied smoothly relative to those observed in case 1. When in the off cycle, the temperature and pressure of the refrigerant within the condenser drops continuously. However, when the temperature of the refrigerant within the condenser becomes almost equivalent to the environmental/ambient temperature, the flow of the refrigerant at discharge of the condenser becomes the major determinant of the changes evident in the refrigerant temperature. Thus, the flow rate of the refrigerant drops as the differential pressure between the condenser and the evaporator decreases, which in turn stimulates heat transfer that brings about the temperature equilibrium attained between the inner and outer part of the condenser; this explains why the refrigerant temperature profile that was obtained at the condenser outlet appeared concave and the temperature outside the condenser was found to be greater than the minimum attainable temperature. In case l, the liquid refrigerant flows through the capillary tube from the condenser into the evaporator after shut-down. By estimation, the refrigerant within the condenser accounts for about 20 % of the total charge after migration. However, the situation is the reverse of the occurrence in Case2, where the liquid is domicile in the condenser. At compressor initiation/startup, the evaporation temperature drops at a faster pace. Thus, as a result of the mass flow rate of refrigerant within the capillary tube being

higher than that in the compressor inlet, there is a temperature boost/ gain at the evaporator outlet; this scenario lasts longer in case 2 relative to case 1. For case l, pressure responses are influenced by the flow of the refrigerant and heat transfer. Hence, the final equilibrium pressure is the saturation pressure which corresponds to the outside temperature of the evaporator. However, in case 2, the off cycle pressure change is only affected by heat transfer such that, the pressure of the refrigerant inside the condenser and evaporator is the saturated liquid and vapour pressures corresponding to their outside temperatures respectively, which cannot attain equilibrium under this condition. Hence, the pressure-temperature responses during the on cycle in cases 1 and 2 are somewhat similar and the evaporator pressure after start-up, drops faster in case 2 compared to case 1. Therefore, the cooling capacity may then increase during the on cycle as the liquid becomes fully evaporated in the evaporator. It was observed that after about 80 secs, the inputpower for both cases became equal. Thus, if the refrigerant is prevented from flowing during the off' cycle, the peak value of the inputpower then drops to about 9.4 % while the total power then reduces by 4 % during the on-cycle. At start-up condition, the heat inertia of every part of the equipment imparts on the temperature and pressure thus causing energy loses. The system then approaches steady state earlier by reducing/regulating the inertia-heat which then results in energy conservation. Thus, increasing the inertia-heat of the equipment causes the the pressure and temperature to flatten with a resultant flow of more refrigerant from the condenser to the evaporator during the off cycle as evident in case 1. This then extends/prolongs the start-up operation of the compressor with resultant energy conservation. Thus, in order to avoid the exigencies associated with taking cognizance of the effects of the on and off cycle operation of the compressor during vapor compression, wherein exergy losses become somewhat essential, the calculated compressor enthalpy, entropy and pressure values were drawn at saturation point. However, if the assertions of the authors were to be imbibed, it then implies that the calculated compressor input power experiences 4 % loss, while the peak value is about 9.4 % of the estimated value. In future studies, it is then recommended that the influence of exergy losses on compressor input and output power are incorporated into the unsteady state calculations for a proper guide to the existing/inherent transient responses of the input and peak powers of the compressor, which gives a better/more accurate estimate of the compressor work for the SiNP and CuNP-nanolubricant systems.

Based on the results in Table 5, despite the prospects inherent in the use of the 0.56 M SiNP mixed with 1 M CuNP-oil, it was observed that the lowest attainable temperature is -9 °C which was obtained at 80 kHz sonication of the hybrid-oil system, whereas, that of the 1 M CuNP-oil system still gave the best cooling effect/lowest temperature (-10 °C) at the same sonication-condition. Thus, owing to the closeness of the

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#### Table 5

Performance-summary for comparing hybrid and the best lone nano-oil based systems sonicated at 80 kHz.

Oil system: R134a mixed with:	Lowest possible temperature (°C)
Copeland	-4
0.5 M CuNP-oil	-7
1.0 M CuNP-oil	-10
1.5 M CuNP-oil	-9
0.56 M SiNP-oil	-7
1.29 M SiNP-oil	-4
1.69 M SiNP-oil	-4
0.56 M SiNP and 1 M CuNP-oil	-9

results, the SiNP and CuNP mixed with the Copeland oil can be improvised for the 1 M CuNP-oil system since the difference in their lower limit temperatures is just -1 °C when both oils are used at sonication speeds of 80 kHz. Hence, if a sonication speed of 80 kHz must be maintained, then the 1.0 M CuNP-oil system should be preferred, however, the concentration of copper must be doubled to achieve -10 °C. Note that the effect can be achieved for 0.5 M and 1.0 CuNP-oil systems whose lowest temperature is -11 °C; in this case, it requires less amount of copper i.e., half the concentration of copper to produce the same

cooling effect of -11 °C at a frequency of 120 kHz. Thus, there is need to strike a balance between energy and cost of materials for such operations.

#### COPs of the CuNP & SiNP-oils

Fig. 16a and b show the estimated COPs of the R134a used alongside the pristine non-sonicated Copeland oil and other nano-entrained oil systems. In Fig. 16a, the estimated COPs of the R134a and pristine nonsonicated Copeland, the 0.56 M SiNP-Copeland oil, 1.29 M SiNP-Copeland oil and 1.69 M SiNP-Copeland oil (selected oils as those presented in Table 5) were plotted at different times. The recorded COPs are in the range of 4.5-3.8 for the R134a and pristine non-sonicated Copeland oil, whereas, the values ranged from 4.9 to 3.9 for the 0.56 M SiNP-Copeland oil, 4.6-3.6 for the 1.29 M SiNP-Copeland oil and 4.5-3.5 for the 1.69 M SiNP-Copeland oil when the oils were sonicated at 120 kHz; these results are in line with the findings of Subramani et al. [70] and Kumar et al. [71]. Although high COPs are indicative of good refrigerator performance, however, the COP of a refrigerator must not exceed its optimum value where the refrigerator must have attained its best conditions of performance, such that, any alteration or deviation in COP from the optimum value can cause a drop in the performance of the refrigerator; some authors have proven that the highest attainable COP



а



Fig. 16. CoP vs pull down time for the pristine (non-sonicated/non-nano-doped Copeland oil and: a. SiNP-Copeland oil, b. CuNP-Copeland oil sonicated at 120 kHz Note: The pull down time-temperature curves alongside the COPs were obtained using a constant weight of the nanoparticles i.e., 1.5 g of nanoparticles in oil.

of a refrigerator does not essentially correlate its condition of best performance because of issues associated with compressor work and efficiency [17]. Here, amongst the Si-doped Copeland oils, it is obvious that the oil system for which the refrigerator had its highest coefficient of performance is the 0.56 M SiNP-Copeland oil system, nonetheless, the COP dropped lower than that of the non-sonicated oil system after 18000 s. In a similar study, 0.5 vol% Cu-Ag alloy and CuO nanolubricants gave COP increments of 20.88 % and 14.55 % respectively, compared to that of the pristine compressor oil owing to the enhanced tribological properties of the oil by the nanoparticles [51]; these observations are in line with the findings of this study where about 9 % increase in COP was recorded for the CuNP and SiNP-nanolubricant due to the improved tribological properties (apparent viscosity, lubricity and yield stress) imposed by the CuNP and SiNPs in the lubricant/Copeland oil. The difference in the results may be as a result of the difference in the nature of the oils and nanoparticles.

Fig. 16b shows the profile of the estimated COPs of the R134a used alongside the pristine non-sonicated oil system mixed with the CuNPentrained oil systems and the CuNP mixed with SiNP-nanoparticulate hybrid oil system. The estimated COPs are in the range of 4.5–3.7, 5.2–3.5, 4.8–3.7, 4.8–3.7 and 5–3.5 for the R134a used with the pristine non-sonicated Copeland oil system mixed with: 0.5, 1, 1.5, as well as the 1 M CuNP-0.56 M SiNP-oil systems respectively, whereas, for the SiNPoils, the COPs were in the range of 4.9–3.6, 4.5–3.5 and 4.5–3.5 for the 0.56, 1.29 and 1.69 M oils respectively; the increase in the highest COP (5.2) over the pristine oil-R134a system is about 16 % which is close to the increased COPs recorded in ref. [51]. Hence, the CuNPs imposed higher COPs in the lubricant as a result of a modification in the tribological properties of the oil.

#### SEM-EDX and FTIR analyses

The SEM, EDX and FTIR spectra of the CuNP and SiNPs are as shown in Fig. 17(a-c), Fig. 18(a,b), Fig. 19(a,b), Fig. 20(a-c), Fig. 21(a-c) and Fig. 22(a-c), and Tables 6-11 which reveal the elemental compositions and distributions of copper in the 0.5 M CuNP-, 1.0 M CuNP, 1.5 M, 0.56 M SiNP-, 1.29 M SiNP, 1.69 M SiNP-oils and the hybrid (1 M CuNP-0.56 M SiNP-oil) sample. The smallest sized particles of highest atomic wt% of each particle-type are those of the 0.5 M CuNP, 1.0 M CuNP and 0.56 M SiNPs which also have very high concentrations of copper 91.03 %, 92.36 % and 34.03 % concentration of silicon, hence, the reasons for their better performances relative to their other counterparts. For the CuNPs, the elemental composition include: Cu, Si, Fe, Ag, Mn, V, Cr, Ti, Ca, Cl, Na, Al, Nb, S, K, Y, Mg, P and C, while elements such as Si, Fe, K, Al, Mg, Ca, Ag, Y, Nb, Co, S, C, Na and P were seen in the 0.56 M SiNPs and 1.65 M SiNPs whereas, only the 1.29 M SiNPs have in addition to the already listed elements, Ti, V and Cr.

In Fig. 17c, for the 0.5 M CuNP-oil, the absorption bandwidth at the 3717.21 cm<sup>-1</sup> peak shows a medium sharp peak of OH-free stretching alcohol; at the 3448.63 cm<sup>-1</sup>, is a peak of strong intermolecularly bonded OH-stretching alcohol, whereas, at the 2858.62 cm<sup>-1</sup> peak, are weak broad intermolecularly bonded OH-stretching alcohols and strong broad NH-stretching amine salts. At the 2442.90 cm<sup>-1</sup> band-width, no visible peak was observed. For the peak at the 2165.75  $\rm cm^{-1}$  mark, strong S-CEN stretching thiocynate bonds and strong stretching amide bonds (N $\equiv$ N = N) were observed; at the 1897.18 cm<sup>-1</sup> peak, weak C-H bending aromatic compounds were suspected, whereas, the flat ends at the: 1602.88, 1560.03 and 1371.45 cm<sup>-1</sup> showed no visible component. At the 960.02  $\text{cm}^{-1}$  peak, strong C=C bending monosubstituted alkenes were seen, while for the peak at the 725.73–667.15  $\text{cm}^{-1}$  mark, strong bending C=C cis-distributed alkenes were observed. At the 494.29 and 451.44 cm<sup>-1</sup> absorbance band-widths, no visible peaks were identified. In Fig. 18c, for the 1 M CuNP-oil, the peak seen at the  $3831.49 \text{ cm}^{-1}$ wavelength, show medium sharp O-H stretching free alcohols. Whereas, for the peak showing at the 3448.63  $\text{cm}^{-1}$  mark, strong broad O=H stretching intermolecularly bonded alcohols were identified. At the 1882.89 cm<sup>-1</sup> bandwidth, are weak C—H bending overtones of aromatic compounds while at the 1154.31 cm<sup>-1</sup> wavelength, the peaks obtained show strong C-F stretching fluoro-compounds; similar peaks were also observed for the 1.5 M CuNP-oil system as seen in Fig. 18c, hence, there was no "c' component graph presented for Fig. 19 in order to avoid any form of duplication.

In Fig. 20c, for the peak seen at 3900 cm<sup>-1</sup>, medium sharp stretching alcohols were identified, while for the peak showing at the 3500 cm<sup>-1</sup> wavelength, medium N—H stretching primary amines were detected. Furthermore, at the 2800 cm<sup>-1</sup> wavelength, strong broad N—H stretching amine salts were detected, while at the 1850–1950 cm<sup>-1</sup> peak, weak stretching C—H aromatic compounds were seen with some measures of overtones.

Considering Fig. 21c, the peaks observed at the 3900, 3483.63, 2700, 1950–1850 and 1500 cm<sup>-1</sup> marks show, medium sharp O—H free stretching alcohols, strong broad stretching intermolecularly bonded O—H groups/alcohols, weak broad stretching intramolecularly bonded O—H groups/alcohols, overtones of weak C—H bending aromatic compounds and strong N—O stretching nitro-compounds, respectively.

For the hybrid oil comprising of 1 M CuNP and 0.56 SiNP-oil, there were visible peaks at the 3900, 3500, 1950–1850, 1400 and 1200 cm<sup>-1</sup> marks, which comprise of medium sharp O—H free stretching groups that suggest the presence of alcohols, medium N—H stretching primary amines, overtones of weak C—H bending aromatic compounds, medium COO-H bending carboxylic acids and no visible product respectively (Fig. 22d). Based on all the FTIR plots discussed, it is clear that the oils had similar properties, however, a few variations were evident in the different oils due to the concentration of the particles and the levels of interactions inherent in the fluid-particle mixtures. Figs. 17 and 18(a-c) and Figs. 19–21a-c are the SEM, EDX and FTIR profiles of the 0.5–1.5 M CuNPs/their oils, and the 0.56–1.69 M SiNPs/their oils respectively.

#### SEM-EDX and FTIR data

Table 12 shows the estimated thermodynamic properties of the nanooils. Based on the estimated enthalpies, it is clear that the 1.0 M Cu-Copeland oil had the highest pressure drop (208.14 bar) amongst all the copper entrained oils while the 1.5 M Cu-Copeland oil gave the least pressure drop (187.01 bar); this then confirms the reason why the 1.0 M Cu-Copeland oil also gave the overall best cooling effect of -11 °C amongst all the copper doped oils since pressure is directly proportional to temperature for systems undergoing vapour compression and expansion; the results are in conformance with the findings of Hu et al. [37]. However, for the silicon-doped oils, the oil with the lowest silicon concentration (0.56 M) and highest enthalpy, gave the best cooling effect of -10 °C at 120 kHz (this result is in agreement with that of ref. [28]); this reverse behaviour of the silicon-oil with respect to copper-oil is due to the fact that despite that silicon belongs to group 4 whose elements are not highly reactive, the concentration of copper relative to silicon in the oils would have resulted in copper (a group 3 element) being more conductive relative to silicon, although both are transition metals with comparative conductive properties. Furthermore, the enthalpies of the nano-oils increased all-through; the entropy changes were highest i.e., 0.789 and 0.766 J/kg for the best copper (1 M-CuNP) oil and silicon (0.56 M SiNP) oil respectively. It then suffices to say that the CuNP and SiNPs imposed higher enthalpies in the Copeland oil which then informs higher heat transfer inducement in the oils for efficient expansion and refrigeration.

Table 13 reveals the characteristics of the CuNPs and SiNPs. Based on the results, considering particles of both kinds, the smallest particles i.e., the 1 M CuNPs and 0.56 M SiNPs with the smallest surface areas of 10.3 and 27.75  $\text{nm}^2$  gave the best cooling effects with the R134a refrigerant and are more advantageous in the refrigeration system. Also, the particles were seen to be circular or round with estimated sizes in the range of 2.04–7.1 nm for the CuNPs while the recorded sizes ranged from 3.35 to 29.35 nm for the SiNPs. However, from the work of Sanni et al. [17],





Fig. 17. a. SEM image of the 0.5 M CuNPs, b. EDX profile of the 0.5 M CuNPs, c. FTIR of the 0.5 M CuNP-Copeland.



Fig. 18. a. SEM image of the 1.0 M CuNPs, b. EDX profile of the 1.0 M CuNPs, c. FTIR of the 1.0 M CuNP-oil.

с





Fig. 19. a. SEM image of the 1.5 M CuNPs, b. EDX profile of the 1.5 M CuNPs.

particles with small surface areas per unit volume improved the properties of the synthetic oil used as compressor oil which in turn enhanced the performance of the refrigerator. Furthermore, considering the high reactivity of copper as well as its particle size, it is clearly evident why the 1 M CuNP-oil system gave the best results amongst all the particles considered. From the statistical point of view, the estimated standard deviations which range from 3.04 to 15.71 for the CuNPs and 2.79–8.23 for the SiNPs (Table 13) are measures of the estimated accuracy, reliability and repeatability of the results obtained in this study since every data was generated in triplicate and the average value was recorded for



Fig. 20. a. SEM image of the 0.56 M SiNPs, b. EDX profile of the 0.56 M SiNPs, c. FTIR of the 0.56 M SiNP-oil.



b

Fig. 21. a. SEM image of the 1.29 M SiNPs, b. EDX profile of the 1.29 M SiNPs, c. FTIR profile of the 1.29 M SiNP-oil.



Fig. 21. (continued).

each set of data generated.

Tables A.1-A.6 (Supplementary File) contain: molarities of the synthesized CuNP solutions, molarities of synthesized SiNP solutions, sample-data for the conventional R134a running on pristine Compressor oil taken at 5 h, densities of the CuNPs at different temperatures, densities of the SiNPs at different temperatures, standard enthalpy-entropy data for vapour compression systems at different temperatures and pressures respectively, while Tables A7-A22 show: Some measure of uncertainties in the measured parameters;T-P-t data for R134a and the pristine Copeland oil; T-P-t data for 0.5 M CuNPs mixed with pristine Copeland@40kHz and R134a; T-P-t data for 0.5 M CuNPs @80/120kHz with pristine Copeland and R134a; T-P-t data for1 M CuNPs @40kHz mixed with pristine Copeland oil alongside R134a; T-P-t data for 1 M CuNPs @80/120kHz mixed with pristine Copeland and R134a; T-P-t data for 1.5 M CuNPs @40kHz mixed with pristine Copeland alongside R134a; T-P-t data for 1.5 M CuNPs @80 /120kHz mixed with pristine C46B alongside R134a; T-P-t data for 0.56 M SiNPs mixed with C46B and R134a; T-P-t data for 0.56M SiNPs mixed with Copeland 46B@80/ 120kHz and R134a; T-P-t data for 1.29 M SiNPs mixed with C46B and R134a; T-P-t data for 1.29 M SiNPs mixed with Copeland 46B@80/ 120kHz alongside R134a; T-P-t data for R134a and 1.69 M SiNPs mixed with C46B@40kHz; T-P-t data for 1.69M SiNPs mixed with Copeland 46B@80/120kHz alongside R134a as well as T-P-t data for 0.56 SiNPs and 1 M CuNPs mixed with C46B alongside R134a.

#### Effect of nanoparticles on compressor-life

#### Friction, abrasion and wear

The lubricity of a compressor oil is a measure of its reduction in wear or friction on the compressor. Hence, the lower the lubricity coefficient of a nanofluid, the better is its lubricating ability or wear-resistance. Sanni et al. [17] observed that for two nano-oils (AgNP-Copeland 46B and CuNP-Copeland 46B oils), their lubricating characteristics were of better quality relative to that of the pristine Copeland oil. Thus, according to their investigation, since the coefficient of friction of any oil, is the ratio of the kinetic force exerted on the oil to the normal force or weight of a lubricant, which equals the compressor-torque, therefore, the estimated torques were in the range of 15.6–18.0 Nm with corresponding lubricity coefficients of 0.119–0.154 for the CuNP-oil, 0.134–0.155 for the AgNP-oil and 0.156– 0.180 for the Copeland 46B oil, which are in agreement with the lubricity values of 0.141, 0.151 and 0.154 that were recorded for C37, C79 and C124 oils respectively, and according to them, this in turn imparted improved wear reduction, minimal abrasion with low friction on the compressor [72]. Although the lubricity coefficient had a better improvement (i.e., ranging from 0.1 to 0.151 and 0.117–0.153 for the SiNP- and CuNP-oils respectively) (Table 14) over the results reported by Sanni et al. [17], the results were seen to be in good agreement with the findings of this study. This then informs that the CuNP and SiNPs doped in the lubricant used with R134a, provided a reduction in wear, friction and abrasion of the compressor parts for lower lubricity coefficients and lower torques towards ensuring improved COPs for improved compressor work.

Nanoparticles dispersed in oils are additives which infuse physicochemically unique properties in compressor oils [6,73–82]. Nanometals/particles are characterized by some amount of shear stresses, melting points and ductility, hence they have the ability to serve as friction modifiers and anti-wear agents with self-repairing abilities. Literature has it that, lubricants doped with copper nanoparticles (CuNPs) have caught the attention of several researchers as a result of their excellent properties, and these include small particle size, high melting point and ductility [6,77,81–84] which then complement the reason for selecting Si and Cu for this research whose melting points are 1414 and 1085 °C respectively.

Uflyand et al. [1] discovered that CuNPs helped to modify the tribological properties (i.e., low wear and friction) of a lubricant for efficient lubrication and better compressor performance compared to the neat oil without any nanoparticle. In their study, they found that when 0.2 wt% CuNPs were dispersed in two base fluids and mixed with synthetic SAE 5 W40 oils. The reduction in friction and wear were less than 13 % for the oils [37]. However, they allotted such change (i.e., reduction in wear and friction) to be due to the formation of boundary-films caused by the interaction of CuNPs on friction surfaces which in turn improved the tribo-efficiency.

In the study by Sanni et al. [17], the estimated lubricity coefficients





b

Fig. 22. a. SEM image of the 1.69 M SiNPs, b. EDX profile of the 1.69 M SiNPs c. FTIR of the 1.69 M SiNP-oil, d. FTIR of the Hybrid (0.56 M SiNP and 1 M CuNP-oil) sample.

corresponded to friction/wear reduction ranging from 14.4 to 23.7 % which are higher than the values reported in ref. [37] but were seen to be very close to those measured for the CuNP-oil system and higher compared to those obtained for the SiNP-oil system reported in this

study (Table 14); this confirms the superiority of the 0.56 M SiNP-Copeland oil system in this regard which is somewhat responsible for the better performance of the refrigerator for the 0.56 M SiNP-oil. Based on the investigation conducted by Padgurskas et al. [36], the





tribological properties of individual and combined Fe, Cu and Co in mineral oil, revealed that Cu gave the best friction and wear reduction of 49 % compared to Fe and Co whose values were 39 and 20 % respectively. Even in their combinations, the hybrid Fe-Cu gave 53 % reduction in friction relative to 36 % as recorded for the Fe-Co which is in close agreement with the highest value obtained (35.9 %) for the 0.56 M SiNP-oil. However, variations in the estimated friction/wear reduction values can be attributed to the type of mineral/synthetic oil used, sizes of the synthesized nanoparticles, the methods of dispersion/mixing adopted as well as the viscosity and densities of the oils.

According to Kumara et al. [13], the inclusion of AgNPs modified by thiolated ligands of 4-(*tert*-butyl) benzylthiol, and dodecanethiol in a base oil caused 35 and 85 % reduction in friction and wear respectively during compressor-lubrication. It is also clearly evident that, the friction reduction value obtained in their study is very close but slightly lower than the upper limit (35.9 %) of friction reduction obtained in the current study, and this could have been due to the difference in the nanoparticles (i.e., AgNPs) used in their study compared to those of the SiNPs/CuNPs used in the current study. Other reasons include the oil type/properties, flow rate and the nature of interactions between the

nanoparticles and the compressor oils. They also asserted that frictionand wear-reduction are largely due to the inherent lubrication mechanisms on the components of the compressor, which include the formation of adsorbed tribo-films that helped in the modification of surface properties of the oils by inducing additional tribological characteristics which may have led to the formation of a film between the rubbing surfaces thus resulting in minimal or negligible abrasion [85–87]. Their results also suggest that, for the nanolubricant and R134a system used in this study, the added CuNP and SiNPs in the compressor oil were frequently trapped and rolled into smoother powders and adsorbed tribo films within the compressor motor with a resultant rubbing effect that brought about induced reduction in friction and compressor-wear. Thus, at the instance of wear, nanoparticle -compaction along the wear-track, is redressed by a sintering behaviour or repair-effect (minimal abrasion), which is aided by the generated heat and pressure during friction [88,89]; this then further confirms the suitability of the SiNPs and CuNPs adopted as friction modifiers for the compressor oil used in this study. However, owing to the larger particle size of the 0.56 M SiNPs in terms of the estimated COPs, the 0.56 M SiNP-oil, did not give a better performance compared to the 0.5 M CuNP and 1 M CuNP-oil. However,

### Table 6

Elemental distribution of the 0.5 M CuNPs.

Element number	Element symbol	Element name	Atomic Conc.	Weight Conc.
29	Cu	Copper	86.86	91.05
14	Si	Silicon	2.61	1.21
26	Fe	Iron	1.19	1.09
47	Ag	Silver	0.43	0.77
25	Mn	Manganese	0.77	0.70
23	V	Vanadium	0.76	0.64
24	Cr	Chromium	0.70	0.60
22	Ti	Titanium	0.74	0.58
20	Ca	Calcium	0.74	0.49
17	Cl	Chlorine	0.67	0.39
11	Na	Sodium	0.97	0.37
13	Al	Aluminum	0.81	0.36
41	Nb	Niobium	0.23	0.36
16	S	Sulfur	0.63	0.33
19	K	Potassium	0.46	0.29
39	Y	Yttrium	0.20	0.29
12	Mg	Magnesium	0.54	0.22
15	Р	Phosphorus	0.37	0.19
6	С	Carbon	0.32	0.06

1	Tal	ble	7
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# Elemental distribution of the 1.0 M CuNPs.

Element number	Element symbol	Element name	Atomic Conc.	Weight Conc.
29	Cu	Copper	86.92	92.36
14	Si	Silicon	6.89	3.24
47	Ag	Silver	0.37	0.66
20	Ca	Calcium	0.92	0.61
41	Nb	Niobium	0.32	0.49
19	К	Potassium	0.70	0.46
17	Cl	Chlorine	0.71	0.42
16	S	Sulfur	0.76	0.41
13	Al	Aluminum	0.86	0.39
39	Y	Yttrium	0.21	0.32
22	Ti	Titanium	0.27	0.22
11	Na	Sodium	0.47	0.18
12	Mg	Magnesium	0.33	0.14
23	V	Vanadium	0.09	0.08
6	С	Carbon	0.19	0.04
15	Р	Phosphorus	0.00	0.00
25	Mn	Manganese	0.00	0.00
26	Fe	Iron	0.00	0.00
24	Cr	Chromium	0.00	0.00

# FL

Table 11

Element number	Element symbol	Element name	Atomic Conc.	Weight Conc.
14	Si	Silicon	41.13	33.84
26	Fe	Iron	12.02	19.66
19	K	Potassium	9.66	11.07
13	Al	Aluminum	12.39	9.80
12	Mg	Magnesium	10.02	7.13
20	Ca	Calcium	3.73	4.37
47	Ag	Silver	0.99	3.13
27	Со	Cobalt	1.21	2.09
41	Nb	Niobium	0.72	1.95
39	Y	Yttrium	0.62	1.61
17	Cl	Chlorine	1.26	1.31
6	С	Carbon	3.54	1.25
16	S	Sulfur	1.24	1.16
25	Mn	Manganese	0.50	0.81
15	Р	Phosphorus	0.69	0.63
11	Na	Sodium	0.29	0.20
22	Ti	Titanium	0.00	0.00
23	V	Vanadium	0.00	0.00
24	Cr	Chromium	0.00	0.00

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Table 9 Elemental distribution of the 0.56 M SiNPs.

Element number	Element symbol	element name	Atomic Conc.	Weight Conc.
14	Si	Silicon	41.61	34.03
26	Fe	Iron	13.82	22.48
19	K	Potassium	10.61	12.08
13	Al	Aluminum	13.73	10.79
12	Mg	Magnesium	10.20	7.22
20	Ca	Calcium	3.52	4.11
47	Ag	Silver	0.75	2.35
39	Y	Yttrium	0.62	1.60
41	Nb	Niobium	0.47	1.26
27	Со	Cobalt	0.52	0.90
16	S	Sulfur	0.73	0.69
6	С	Carbon	1.68	0.59
11	Na	Sodium	0.28	0.19
15	Р	Phosphorus	0.15	0.14
22	Ti	Titanium	0.00	0.00
23	V	Vanadium	0.00	0.00
24	Cr	Chromium	0.00	0.00

Table 10		
Elemental distribution	of the 1.29 M Si	VPs.

Elemental distribution of the 1.69 M SiNPs.

Element number	Element symbol	Element name	Atomic Conc.	Weight Conc.
14	Si	Silicon	39.96	32.27
26	Fe	Iron	13.40	21.51
19	K	Potassium	10.91	12.26
13	Al	Aluminum	12.95	10.04
12	Mg	Magnesium	10.03	7.01
20	Ca	Calcium	3.78	4.36
47	Ag	Silver	0.90	2.79
41	Nb	Niobium	0.64	1.71
39	Y	Yttrium	0.50	1.28
27	Со	Cobalt	0.59	0.99
22	Ti	Titanium	0.61	0.84
16	S	Sulfur	0.87	0.81
23	V	Vanadium	0.54	0.80
17	Cl	Chlorine	0.77	0.79
25	Mn	Manganese	0.48	0.75
6	С	Carbon	1.89	0.65
24	Cr	Chromium	0.33	0.50
11	Na	Sodium	0.48	0.32
15	Р	Phosphorus	0.35	0.31

# Table 8

Elemental distribution of the 1.5 M CuNPs.

Element number	Element symbol	Element name	Atomic Conc.	Weight Conc.
29	Cu	Copper	78.99	86.66
14	Si	Silicon	8.34	4.04
16	S	Sulfur	2.40	1.33
26	Fe	Iron	1.00	0.97
47	Ag	Silver	0.43	0.80
23	V	Vanadium	0.78	0.69
20	Ca	Calcium	0.99	0.69
25	Mn	Manganese	0.70	0.67
41	Nb	Niobium	0.39	0.63
22	Ti	Titanium	0.71	0.59
11	Na	Sodium	1.38	0.55
19	K	Potassium	0.75	0.50
17	Cl	Chlorine	0.78	0.48
24	Cr	Chromium	0.49	0.44
39	Y	Yttrium	0.20	0.30
13	Al	Aluminum	0.64	0.30
12	Mg	Magnesium	0.35	0.15
15	P	Phosphorus	0.24	0.13
6	С	Carbon	0.42	0.09

#### Table 12

Thermodynamic properties of the nano-compressor fluids.

Comp	Conc (M) @ T1(P1), T2(P2)	$\Delta P$ (bar)	∆vCp (J/g)	∆liqCp (J∕ g)	ΔT (T1-T2) (°C)	∆h (J/kg)	m*∆h (J)	∆s J∕g	m*∆s J	Mp g	m. flow
CuNPs	0.5 @ 11(428.63), -7(225.48)	203.15	0.086672	0.0507	18	203.81	2527.24	0.766	9.5	12.4	2.48
	1.0 @ 9(400.94), -11(192.8)	208.14	0.09005	0.054	20	206.68	5146.33	0.789	19.64	24.9	4.98
	1.5 @ 8(387.61), -10(200.6)	187.01	0.08097	0.0485	18	205.96	7702.90	0.783	29.28	37.4	7.48
SiNPs	0.56 @ 0(292.8), -7(225.48)	67.32	0.03051	0.0181	7	203.81	13969.	0.766	52.48	68.54	13.71
	1.29 @ 11(428.63), -4(252.68)	175.95	0.07113	0.0432	15	197.6	27087.01	0.749	102.68	137.08	27.42
	1.69 @ 12(443.01), -5(243.34)	199.67	0.08068	0.0489	17	202.34	46974.08	0.755	174.80	231.66	46.33
Si and Cu-NPs	0.5 + 1.0 @ 9(443.01), -9	234.37	0.08193	0.0492	18	205.25	19178.56	0.777	72.61	93.44	18.69
	(208.64)										
Copeland46B	@10(414.61, -4(252.68)	161.93	0.09086	0.0400	14	201.6	7963.2	0.749	29.59	39.5	7.9

Key: Comp - components; Conc. - concentration (M); T1, T2 ( $^{\circ}$ C), are the initial and final temperatures; P1, P2 (bar) are the initial and final pressures;  $\Delta P$  - pressure change;  $\Delta v$  Cp - change in specific heat capacity of vapour;  $\Delta liq$ . Cp - change in specific heat capacity of liquid;  $\Delta T$  - temperature change; Mp - mass of particles or oil; m.flow - mass flow rate of compressor oil;  $\Delta h$  - enthalpy change of oil @ the final temperature; m. $\Delta h$  - product of mass of particle-oil mix or oil and enthalpy change of liquid/oil per unit mass;  $\Delta s$  - change in liquid/oil entropy per unit mass; m. $\Delta s$  - product of mass of particle in oil and the entropy change per unit mass. Time taken for the experiment is 5 h.

#### Table 13

Characteristics of the nanoparticles as analyzed from SEM images by image J software.

Nanoparticles	Concentration (M)	Area (nm <sup>2</sup> )	Particle diameter (nm)	Shape	Standard deviation
CuNPs	0.5	39.6 10 3	7.1 2.04	Circular/round	15.71 8.04
	1.5	15	2.47	Circular/round	3.04
SiNPs	0.56 1.29 1.65	27.75 59 2126.67	3.35 4.89 29.35	Circular/round Circular/round Circular/round	8.23 7.69 2.79

### Table 14

Lubricity coefficients of the nano-Si and Cu-Copeland oils at varying torques and speeds.

Torque (Nm)	Motor Speed (RPM)	Lubricit 1 M Si 1	y Coefficient (-) 1 M Cu Copeland	Friction Reduction by change in lubricity (SiNP-oil:CuNP-oil) %	
15.6	30	0.10	0.117	0.156	35.90:25.0
16.0	60	0.121	0.123 (C120 fuel 0.26)	0.160	24.38:23.13
16.5	100	0.133	0.137	0.165	19.39:16.97
17.5	200	0.138	0.140 (C39 fuel, 0.141)	0.175	21.14:20.0
18.0	400	0.151	0.153 (C40 & C126 Fuels: 0.154)	0.180	16.11:15.0

\* C39-C126 fuel characteristics as determined by Arkoudeas et al. [71] compared favourably with those of the 0.56 M SiNP and 1 M CuNP nano –oils. The coefficient of friction or lubricity values measured for B100SB, B20SB and B10SB oils, whose values range from 0.1 to 0.21 (Mendes de Farias et al. [46]) are in good agreement with the estimated lubricities of the 0.56 SiNP and 1 M CuNP oils.

the latter being better conductors is also another reason for the variations observed in their estimated enthalpies (Table 12).

# Environmental impact/safety and recyclability potential of the best SiNP and CuNP-oils

Silicon being a useful metal is ecofriendly at low concentrations however, at high concentrations, the metal may be somewhat harmful to the environment. Hence, since the best SiNP doped lubricant i.e., the 0.56 M SiNP-oil contains Si which is nonbiodegradable, the option of recycling the oil may be considered in order to enhance its reusability. Thus, when its reusability or cycle-span is fully exhausted, options for adopting the oil as base oil for fresh lubricants may become essential so as to abate the option of dumping the oil in the environment which may in turn influence soil pH. By this, sustainability is ensured within possible considerations for a circular economy. In addition, literature has it that, Si can be used for medical, cosmetic, cooking and electrical purposes [90], hence, moderate concentrations of the metal should be used for energy systems as presented in this study. Some literature also posit Si as being a natural occurring element that is non-toxic [90], this then suggests that rapt attention should be paid to the concentration of Si if it must be used, because, this is what determines how safe or harmful it may be. In this study, the concentration of Si adopted spans from 0.56 to 1.69 M which is non-toxic to the environment and humans.

#### Nanoparticle-effect on Compressor-work, safety and performance

Based on the study by Sanni et al. [17], a better energy consumption/ performance was recorded for the 1.1–2.1 M CuNP-oils whereas, very low compressor performances were obtained for the 0.02–0.08 AgNPoils in terms of energy transmission; this then confirmed the superiority of the copper-doped Copeland oils relative to the AgNP-oils in terms of work done by the compressor. Lower compressor work within the threshold limit of compressor performance improves the lubricity and friction reduction on a compressor with resultant enhancement in its performance; this observation is in accordance with the findings of the current study.

The higher enthalpies of the CuNP-oils relative to the SiNP-oils are due to the higher thermal conductivity of copper (360–400 W/mk) compared to that of Si which is 148 W/mK. For nanoparticles of similar kind, part of the factors affecting the heat distribution in a system of two miscible components is the solute-concentration. Smaller particle sizes result in faster reaction-rates with higher amounts of heat absorbed by the reactants as experienced in the case of the SiNPs, where it is evident that the size of the 0.56 M SiNP was larger relative to that of the 1 M CuNP; this also corresponds to lower surface area to volume ratio of the SiNP relative to the CuNP which is a major factor that slows/speeds up a system's performance i.e., higher surface areas to volume ratios give higher performances and vice versa. Furthermore, owing to the lower density of Si relative to Cu, the former diffuses faster and travels faster when both particle-types are present in a fluid; this is the reason SiNPs impose better lubrication properties in the oils, whereas, in terms of the estimated COPs, the 1 M CuNP-oil performed better.

Considering the work of Maidul-Islam and Mukar-Jee, [26], less than 20 % vol CuNPs possesses a characteristic hydrodynamic diameter of about 10 nm at 25 °C whereas, the hydrodynamic diameter was 20 nm for 20, 40, 70, 90 and 120 %vol concentrations of CuNPs and this has a way of influencing the performance of these oils. However, despite the fact that hydrodynamic diameter of Si in a serum, ranges from 166 to 1170 nm, the lower density, higher surface area to volume ratio and higher specific heat capacity of Si (i.e., 0.71 compared to 0.38 W/mk) are the reasons the results are in variance with those obtained in ref. [26] i.e., one would expect the CuNP-oil to perform better owing to its lower hydrodynamic diameter. Another factor that may have resulted in the lower enthalpies of the SiNP-oil system is the higher specific heat capacity of Si i.e., the amount of heat required to raise the temperature of 1 g of Si is higher relative to that required to raise the temperature of the same mass of Cu. In other words, the heat gained by 1 g of CuNPs as compared to SiNPs of same mass for 1 K rise in temperature, is higher for Si relative to Cu, meaning, Cu can withstand higher temperatures owing to its higher thermal conductivity and thus preserves the compressor-life better than Si. Since the specific heat capacity of silicon is 1.87 times that of Cu, for a unit mass of each particle, it then implies that the effect becomes seemingly cumulative thus favouring SiNPs when a number of these particles appear in polydisperse phase or are suspended in a fluid medium. Si has higher thermal resistance relative to Cu which is evident in their thermal conductivity (see Fig. 9a). According to ref. [26], at higher temperatures, nanoparticles may become less dispersed in some oils or polymeric fluids such as Polyethylene oxide (PEO).

#### New generation nanolubricants for refrigeration application

According to Unilab Srl, a heat transfer software development company, some researchers have proposed the introduction of a new wave in refrigeration tagged, "nanorefrigertion"; this involves the blending of nanoparticles such as NiFe2O4, TiO2, Al2O3 in mineral/ synthetic oils. The study by Bi et al. [91] improvised polyol-ester with a mineral oil mixed with  $TiO_2$  nanoparticles in a refrigerator that employed R134a as refrigerant. Based on the compatibility, energy consumption and freeze capacity-tests conducted for the nonmetallic components of the refrigerator (265 L capacity, double door with reciprocating compressor) with R134a/POE oil (pristine oil), two R134a/mineral oil-nanoTiO $_2$  separate mixtures (with 0.06 and 0.1 %  $TiO_2$  nanoparticles) and  $Al_2O_3$  of 0.06 and 0.1 % separately added to mineral oil, the results showed that the system had energy consumption (kwh.day) vs saving rates (%) of 1.077 kwh.day vs 0 %, 0.849 kwh.day vs 21.2 %, 0.796 kwh.day vs 26.1 %, 0.826 kwh.day vs 23.2 %, 0.852 kwh.day vs 20.9 % respectively, whereas, over a fifty-day period, the best energy saving oil (i.e., mineral oil-0.1 % TiO2 nanoparticles, demonstrated an overall energy saving capacity of 25.7 % over a fiftyday period of operation. Also, considering the energy saving capacities of the nano-doped compressor oils, it is evident that the energy saving capacity falls within the range of 20.9–26.1 % for all the nanoparticle blended oils as against 16.7 % which was obtained for the pristine mineral oil. Considering the fact that the results are different for different nanoparticle types, it then informs the potentials that underly these substrates as additives for modifying the properties of R134a and the mineral oils used. This improved energy saving rates also translated to lesser emissions resulting from the high miscibility of the R134a and nano-blended mineral oils alongside improved oil return-ratio of the compressor. In the work of Sabareesh et al. [92], 0.01 % TiO<sub>2</sub> was blended in an oil that was used as compressor fluid in a CFC R12 refrigeration system with a measurable GWP of 10900. It was observed that the 0.01 % TiO<sub>2</sub> in the oil, increased the average cooling capacity by 3.6 % with a corresponding reduction in the power input of the refrigerator by about 11 % which in turn resulted in a COP increase of 17 % for the vapour compression system. In another study, Wang et al. [93] showed that a new mineral-based nano-refrigeration oil comprising of

#### Table 15

Cost of	some	refrigerants	alongside	their	GWPs and	ODPs.
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Cost	GWP	ODP
4.65 dollars/ kg	0	0
8.83 dollars/ kg	1	0
2.65 dollars/ kg	1430	0
73.00 dollars/ kg	1	0
8.00 dollars/ kg	4	0
3.73 dollars/ kg	5	0
40.00 dollars/ kg	6	0
10.00 dollars/ kg	122	0
27.39 dollar/kg	124	0
3.50 dollar/kg	466	yes
3.58 dollar/kg	601	yes
	Cost 4.65 dollars/ kg 8.83 dollars/ kg 2.65 dollars/ kg 73.00 dollars/ kg 8.00 dollars/ kg 3.73 dollars/ kg 40.00 dollars/ kg 10.00 dollars/ kg 27.39 dollar/kg 3.50 dollar/kg 3.58 dollar/kg	Cost GWP   4.65 dollars/ kg 0   8.83 dollars/ kg 1   2.65 dollars/ kg 1430   73.00 dollars/ kg 1   8.00 dollars/ kg 1   8.00 dollars/ kg 5   40.00 dollars/ kg 6   10.00 dollars/ kg 122   27.39 dollar/kg 124   3.50 dollar/kg 601

NiFe2O4 nanoparticles mixed with naphthene based oil (B32) can be used to enhance the performance of a R410A residential air conditioner. The solubility analyses conducted for the nanocompressor oil revealed a high measure of miscibility of the nano-lubricant with R134a, R410A, R425a and R407C. Direct studies on the lowering of the GWP refrigerants with high GWP are quite scarce, however, due to the energy saving potentials of these nanoparticles in oils, it is perceived that these particles have the potentials of lowering the GWP/risks associated with refrigerants with higher GWP than 150 as stipulated in the Refrigerant Management Program (RMP) defined in the Code of Federal Regulation (title 40), Part 82, and the IPCC's fourth Assessment Report (AR4) of 2007.

Furthermore, considering the data shown in Table 15, the cost of all new replacements for R134a listed are quite expensive and are yet to be fully available in several nations of the earth which has caused the continuous use of some refrigerants such as R134a despite their high GWPs. Also, some newly supposed alternatives such as opteon XL41, R450A, R-513A, R-452B and R141b, despite having GWPs of 466, 601, 631, 676, 725, unlike R134a, are ozone depleting which gives the latter an advantage over the listed refrigerants. Hence, there is need to search for alternative means of improving/optimizing the properties of R134a for refrigeration applications in view of its zero-ozone depleting potential and high GWP relative to other existing/new and more expensive alternatives which are rarely available in some parts of the world.

# Reasons for the better cooling effects of the CuNP-oil-R134a system relative to the SiNP-oil-R134a system and the pristine Copeland Oil-R134a system

Evidence has it that, for nano-entrained oil-refrigerant systems, the boiling heat transfer coefficient is usually larger relative to that of the system comprising of pure refrigerant and pristine oil [94]. It then suffices to say that for the 0.5-1.5 M CuNP and 0.56-1.69 M SiNP-Copeland oils used with the R134a, the boiling heat transfer coefficient of the refrigerant from the evaporator is higher relative to that of the R134a and the pure Copeland oil, however, that of the 0.5 M/1M CuNP-oil-R134a surpassed the performance of all the oils. Thus, the enhancement ratio of the system comprising the CuNP/SiNP nanolubricants with R134a varied with nanoparticle concentration. The presence of stabilizing/surface active agents on the surface of the CuNP and SiNPs also enhanced the boiling heat transfer performance of the evaporator owing to the decrease in the surface tension of the working fluids, nonetheless, the 0.5 M/1 M CuNP-oil and R134a system, had the best enhancement in their boiling heat transfer performance as well as the lowest surface tension. Consequently, the inherent number of bubble nucleation sites increased for the 0.5 M/1M CuNP-oil and R134 with a corresponding decrease in the bubble departure diameter in lieu of the high bubble departure frequency relative to the other oils; this agrees with the explanation of Wasekar and Manglik [94]. Also, the measure of interactions that ensued between CuNP and SiNPs, the surfactant and the Copeland oil, reduced the surface tension of the working fluids [95]

which may affect the enhancement of the surface active agents present on the surfaces of the SiNPs, thus weakening the performance of the SiNPs and the pristine Copeland oil R13a systems compared to the CuNPs which could have offered higher resistance as a result of higher stability of the CuNP-oil. However, the possibility of the continuous deposition of the nanoparticles during the boiling/evaporation phase gives rise to the tendency for the continuous modification of the surface characteristics of the evaporator throughout the fluid circulation cycle [96]. The subsequent interaction of the 0.5 M/1 M CuNPs in the Copeland oil and the heating surface increased the active nucleation sites which in turn improved the boiling heat transfer performance of the R134a. However, the deposition of the SiNPs, provided some measure of thermal resistance, which diminished their boiling heat transfer performances relative to those of the CuNPs, although, the SiNP-oil and R134a system still gave better performance compared to the pristine Copeland oil-R134a system. Furthermore, thermal resistance is partially responsible for the deterioration of the boiling heat transfer characteristics of the R134a and CuNP/SiNP-oil systems [97]. Despite the increase in the number of active nucleation sites, the lower deterioration factors of the CuNP compared to the SiNP-oils and neat Copeland oil-R134a system, lowered the measure of boiling heat transfer enhancement experienced by the SiNP-oils and R134a systems as well as that of the pristine Copeland oil. Nevertheless, the boiling heat transfer coefficient of the CuNP/SiNP-oils and R134a systems were still higher than that of the pure R134a and pristine Copeland oil system. Under a low heat flux, the deterioration factors may dominate [98] and cause a lower enhancement ratio of the CuNP/SiNP-oil and R134a system relative to that of the R134a. However, under high or increased heat flux, the enhancement factors dominate/prevail, which in turn result in an increase in the enhancement ratio of the 0.5 M/1 M CuNP-oil and R134a system over that of the SiNP/pristine Copeland oil and pure R134a system, thus resulting in maximal heat utilization/transfer during cooling with inherent lower temperatures and higher cooling efficiencies for the 0.5 M/1 M CuNP-oil and R134a system. Another reason for the best cooling efficiency experienced by the 0.5 M/1 M CuNP-oil and R134a systems relative to the SiNP/pristine Copeland oil and R134a system is due to the lower energy consumption of the former relative to the latter, which in turn reduces capillary action towards enhanced COPs [99]. According to Sabareesh et al. [100] the COP of a vapor compression cooling system involving nanolubricants/nanorefrigerants can be enhanced by the modification of physical properties such as viscosity and lubrication characteristics. Also, at optimum particle concentration, the 0.5 M/1 M CuNP-oil's viscosity, friction coefficient as well as the surface roughness of the 0.5 M/1 M CuNPs impart surface properties on the lubricant and R134a owing to their more pronounced uniform dispersion which helps to bring about decreased compressor-work with resultant high heat transfer rates and increased COPs compared to the SiNP/Copeland oils.

Furthermore, in cooling devices, the freezing speed and COP of the vapour compression systems can increase by the inclusion of the optimum concentrations "0.5 M/1 M CuNPs" in the Copeland oil, which subsequently resulted in increased heat transfer rate and pressure drop for the different oils in the order of 0.5 M/1 M CuNP-oil-R134a system > 0.56 M SiNP-oil-R134a system > pure Copeland oil-R134a system. However, the heat transfer rate was highest for the smaller nanoparticle sizes while the pressure drop decreases, thus giving rise to efficient cooling effects and lower temperatures for the 0.5 M/1 M CuNP-oil-R134a system.

In addition, studies have shown that nanoparticle-volume fraction/ concentration in nanofluids have a significant influence on the inherent temperature of a refrigeration/cooling system which in turn affects the viscosity, density and specific heat of the system [101]. Therefore, considering the CuNP/SiNP-nanolubricant and R134a system, the results indicate that viscosity changes were induced by variation in particle concentration, whereas, at the optimum concentration of 0.5 M CuNP in the Copeland oil, the cooling effect of R134a is best enhanced owing to the modified density and lowered specific heat of the fluid. When the density of the nanorefrigerant increases as a result of its interaction with the CuNP/SiNP-entrained lubricants, there is a resultant drop in the the specific heat of the refrigerant (R134a) which then causes a drop in the temperature of the fluid which in turn generates a cooling effect on the system, however, the lowest temperature (-11 °C) was recorded for the 0.5 M CuNP-Copeland oil and R134a system. In addition, the higher thermal conductivity with improved surface areas of the varied concentrations of 0.5-1.5 M CuNP and 0.56-1.69 SiNPs in the Copeland oils, the improved/lower lubricity coefficients that helped to avoid compressor wear, moderation of thermal properties (enthalpy, entropy and specific heat capacity of the lubricant via higher ultrasonication frequencies), moderation of fluid pressure, lower yield stresses and lower densities/viscosity, imposed by the nanoparticles, resulted in improved vapour compression of the R134a and CuNP/SiNP nano-oils which then culminated in efficient energy conservation for improved refrigeration as evident in the high electrical energy conversion to mechanical energy of the compressor and then to heat energy with resultant high cooling efficiencies/high temperature drops. However, the reported properties were more enhanced in terms of the 0.5 M/ 1 M CuNP-oil-R134a system compared to the 0.56 M SiNP-oil-R134a system (which did best among all the SiNP-doped oils) as well as that of the Copeland oil-R134a system which gave the least performance as a result of the unmodified properties of the oil.

# Conclusion

The 0.5 or 1 M CuNP- and 0.56 M SiNP- oils can serve as conventional naolubricants since the entrained nanoparticles are very efficient additives for enhancing the performance of the Copeland compressor oil, which in turn improves the cooling effects of the refrigeration system. The Cu-Copeland 46B oils performed better than the pristine Copeland and Si-Copeland 46B-oils. Variation in frequency from 40 to 120 kHz of the sonicated nano-oils had significant impact on the performance of the Cu-Copeland 46B and Si-Copeland 46B oils with improved thermal conductivities as well as reduced plastic viscosities and yield stresses. In order to ensure high cooling effects, the frequency of sonication of the nano-doped oils must be kept at 80 and 120 kHz, which correspond to upper and lower limit COPs of 5.2-3.5 and 4.9-3.9 for the 1.0 M CuNPoil and 0.56 M SiNP-oil respectively. Higher frequencies of sonication gave comparative COPs and cooling effects, however, the best cooling effect was obtained for the 1 M CuNP-oil whose lowest attainable temperature was - 11 °C. Furthermore, amongst all the Si-Copeland oils tested, the 0.56 M SiNP-oil gave the best cooling effect, although the lowest attainable temperature for this oil system is -7 °C. Also, amongst all the CuNP-oil systems, the 1 M CuNP-oil gave the best performance, especially at 120 kHz. In addition, a blend of the nanoparticles in the Copeland oil gave its lowest attainable temperature as -9 °C which still gives a lower cooling effect relative to the 1 M CuNP-oil system at 80 kHz. This further implies that for optimum refrigerator performance, the pull down time of the vapour compression system running on R134a and the pristine Copeland oil, CuNP-and SiNP- Copeland oils, for the various concentrations of the tested nanoparticles, was found to be 18000 s. It is pertinent to mention here that the refrigerator was not loaded throughout the investigation so that there would be no loss of heat to the items in the chamber; the chamber was left empty all through the experiment. As reported by Sanni et al. [17], at the pull down time of 14400 s, the lowest temperature attained was – 7  $^{\circ}$ C for the 1.6 M CuNP-Copeland 46B oil system, whereas, in this study, the same temperature (-7  $^\circ\text{C})$  was attained in 12000 s for the 0.5 M CuNP-oil 120 kHz, thus comparing both times, it then shows that the time difference (or betterput, time saved in this new study) is 2400 s which equals (0.67 h = 40mins); please see Fig. 14a as evidence (0.5 M CuNP-oil 120 kHz). Again, looking at Fig. 14b, for the C-46B + 1 M CuNPs spun @ 120 kHz, the same temperature "-7 °C", was attained at 14400 s, only that for the modified oil discussed here, sonicating at higher frequency i.e., at 120

kHz relative to 50 kHz as done by Sanni et al. [17], helped to improve the properties of the oil and thus stretched the pull down time towards attaining a lower temperature "–11 °C" which has barely been documented in literature. Good enough, the lowest attainable temperature "–11 °C" for this system was even achieved for a concentration as low as 0.5 M CuNPs in the Copeland oil, this also was not reported by Sanni et al. [17]. Hence, this simply suggests that materials and energy conservation are quite feasible by manipulating the concentrations of nanoparticles sonicated with compressor oils.

The time for which the chamber attained the lowest temperature is about 18000 s which is about 5 h thus, this is not too much time for a single door refrigerator where the compressor power and other factors have a part to play in the overall refrigerator performance in terms of cooling. In essence, this is an indication that the pull down time which is same for all measurements (that is a constant value as usually obtained by other authors i.e., in the region of 14400 s (Sanni et al. [17]; Damola et al. [60]), was only extended owing to the difference in properties of the compressor oil. Furthermore, the point of focus in this study is efficient energy management during refrigeration for optimal cooling efficiency. Although, the lowest attainable temperature in the study of Sanni et al. [17] was – 7 °C, at 14400 s, in this study, the lowest temperature of - 11 °C was achieved, which is the first and best ever recorded in literature; the authors also believe that oil-property modification by nanoparticle intrusion and ultrasonication at higher frequencies may be substantive accountable reasons for the stretch in the pull down time to 18000 s rather than a lower value. Furthermore, it should be noted that the lowest temperature obtained in this study has never been attained or reported by previous literature on the subject, which also reveals the uniqueness of the prepared nanocompressor oils in the refrigeration process. Again, one very interesting result obtained for this system is the fact that the best cooling effect (-11 °C) obtained is thus far, the best ever recorded for refrigeration systems and also stands as an additional contribution to knowledge/significant improvement over those reported in prior studies.

#### Recommendation

Based on the issues related to the on-off cycle of the compressor of a refrigeration unit, it then implies that the calculated compressor input power experiences minimal losses in its input and peak powers during the entire process. Hence, while it is essential to consider such scenario in future studies, it is necessary to understand that carrying this out during the usual experimentation may be herculean but can be tactically done as a separate investigation after taking the temperature-pressure-time data for the entire process. This implies that, the on-off cycle data can be generated as separate experiments in order to determine the influence of exergy losses on compressor input and output power as well as incorporate them into the unsteady state calculations for a proper guide to the existing/inherent transient responses of the input and peak powers of the compressor which gives a better/more accurate estimate of the compressor work.

#### CRediT authorship contribution statement

Samuel Eshorame Sanni: Conceptualization, drafting and revision of original manuscript, methodology, supervision, validation, analyses and project administration. Precious Olofin: Methodology and data curation. Emeka Emmanuel Okoro: Data curation, project administration and visualization. Babalola Oni: Analyses and validation. Agwu Okorie: Data curation and project administration.

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# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

All data used in this research have been included in the manuscript and additional information on the work are available in the supplementary file.

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## Appendix A. Supplementary data

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