



Thermal Conductivity Enhancement of Ternary Organic Heat Transfer Fluids Doped with Al_2O_3 Nanoparticles for Solar Thermal Energy Storage

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Abstract

Thermal Energy Storage (TES) systems are essential for mitigating the intermittency of renewable energy, particularly in Concentrated Solar Power (CSP) applications. This study explores the enhancement of thermal conductivity in novel ternary organic-based TES fluids, composed of varying ratios of oregano oil, olive oil, and castor oil, doped with 5 wt% Al_2O_3 nanoparticles. Using differential scanning calorimetry (DSC), seven undoped formulations were characterized, followed by nanoparticle doping in three selected samples. Thermal conductivity was measured over the range of 300–400 K, yielding values from 0.2886 to 0.5233 W/m·K for undoped samples, with melting points between 333.48 K and 336.21 K. Upon doping, sample SO5 exhibited a 3.7% increase in thermal conductivity, whereas SO2 and SO7 showed decreases of 33.5% and 4.0%, respectively. These results highlight the critical influence of fluid composition, nanoparticle dispersion, and interfacial compatibility on TES performance. This work contributes to the development of cost-effective, high-efficiency TES fluids, offering new pathways for improving the sustainability and performance of CSP systems.

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1. Introduction

Thermal conductivity is a fundamental property that represents the ability of a material to transfer heat across a temperature gradient. The coefficient of thermal conductivity is defined as the rate of transfer of energy across a unit surface area, when there is a unit temperature gradient, dT/dh , perpendicular to the surface. It is measured in watts per meter kelvin (W/mK). Several factors influence the thermal conductivity of a material, including its chemical composition, microstructures, grain size, grain boundary, surface interaction, temperature, and the presence of additives [1-3]. In the case of nanofluids, the thermal properties are dependent on particle size shape ratio, nano-particle mass fraction, the type and composition of the nanoparticles, composition of the base fluid, nanoparticle volume concentration and temperature of both the nanoparticles and the fluid [4-5].

Concentrated solar power CSP technologies can be considered as a sustainable and reliable technology for electricity generation, thus, offering an alternative to traditional fossil fuel power plants [6]. The goal of this transition is to diversify fossil fuels that are detrimental to the environment by emitting harmful gases responsible for climate change and to enhance efficiency [7]. Thermal energy storage (TES) systems offer an effective solution to these challenges, providing cost-effective and minimal environmental impact [6]. In CSP systems, the abundant energy from the sun is harnessed, the solar irradiation is focused onto a receiver: absorber tube, using collector mirrors to increase the temperature of the heat transfer fluid (HTF) [8-11]. The HTFs captures and transports the heat energy [12]. The heat captured can then be used immediately to generate electricity with a steam turbine, or saved for later, which enhances

flexibility and efficiency of the system. The thermal conductivity of HTFs is significantly associated with the performance of CSP systems. Increasing the thermal conductivity of these HTFs is crucial for enhancing overall system performance, focusing on energy production augmentation, and operation cost minimization. CSP technologies can facilitate the shift toward cleaner and more sustainable energy sources by improving HTFs efficiency.

Figure 1 is a schematic diagram of a concentrated solar power (CSP) system [13]. It shows the procedure of collecting solar energy with collector mirrors, which concentrate solar radiation on a receiver (absorber tube), that absorbs and transports thermal energy with the heat transfer fluid (HTF). This retained heat can then be directly utilized in producing power through a steam turbine or stored in a thermal energy storage (TES) system for on-demand use, providing a boost, operational flexibility and efficiency.

Different researchers have investigated the feasibility of organic nanofluids functioning as HTFs in CSP applications. [14] synthesized Al_2O_3 /coconut oil based nanofluids and noted improvements in thermal conductivity with reduction of contact angle up to 70%, which exhibits enhancement in wettability. On the other hand, challenges such as increase in viscosity and nanoparticle agglomeration adversely impacted the flow characteristics of the fluid were also noted. In similar research, [15] studied oil-based hybrid nanofluids composed of coconut and soybean oils with Al_2O_3 - TiO_2 nanoparticle palm oil. Their results claimed the hybridization of nanoparticles improved conductivity, especially in palm oil, but also increased viscosity at low temperatures which restricted flow characteristics. In their studies [16], concentrated on the thermal conductivities of vegetable oils such as rapeseed, soybean, sunflower oil, and palm oil stating that thermal conductivity is dependent on the variation in the fatty acid composition of the vegetable oils used. However, their study did not explore how adding nanoparticles could further improve heat transfer efficiency.

Other studies have investigated nanoparticle-enhanced vegetable oils for non-CSP applications. [17] demonstrated that exfoliated hexagonal boron nitride (h-BN) nanoparticles significantly improved both the thermal conductivity and electrical insulation of vegetable oils used as transformer fluids. However, their application in high-temperature CSP environments remains unexplored. [18] found that incorporating Al_2O_3 and AlN nanoparticles into mineral oil improved thermal conductivity by 18% and 7%, respectively, at specific volume fractions. While their study provides useful insights into mineral oil-based nanofluids, the relevance of these findings to organic-based nanofluids in CSP systems is unclear. Additionally, [19] investigated Jatropa oil enhanced with iron nanoparticles for drilling applications, showing improvements in lubrication and cooling performance. However, their research did not address the performance of such fluids in the high-temperature conditions of CSP systems.

Despite these significant contributions, existing studies highlight several limitations. Many studies fail to consider the full temperature operating conditions required for CSP applications, limiting their applicability. Additionally, most research focuses on single or binary nanofluid systems, whereas ternary nanofluids could offer superior heat transfer properties. Furthermore, although vegetable oils have been explored for heat transfer applications, research on their enhancement with nanoparticles for high-temperature CSP applications remains limited. This study aims to fill these gaps employing ternary organic-based nanofluids doped with Al_2O_3 nanoparticles to promote HTF performance in CSP systems. These novel nanofluids have thermophysical characteristics that can potentially boost heat transfer capabilities, enhance performance thereby achieving high energy conversion efficiency, and promote CSP sustainability.

Selecting the appropriate HTFs with the right dopant is essential for maximizing both efficiency and reliability. Common HTFs used in CSP systems include molten salts, synthetic oils, nanofluids, and gaseous fluids, each with distinct thermophysical properties and temperature operating ranges [10]. Globally, thermal oils account for 92.1% of HTFs in CSP plants, compared to 4.49% for molten salts and 3.37% for water, steam, or air [20 as cited 21]. Thermal oils stand out among these fluids because their low melting points and viscosities which minimize pumping costs and enhance flow dynamics when compared to molten salts. Mineral oils derived from petroleum, synthetic oils made from chemicals and vegetable oils extracted from crops. Synthetic oils, such as biphenyl/diphenyl oxide mixtures are commonly employed in CSP systems operating at a moderate temperature range of 150°C – 400°C [10]. Synthetic and mineral oils serve as heat transfer fluids or thermal storage materials at temperatures above 200°C [21] but pose issues because they are environmentally damaging and expensive while depending on diminishing petroleum reserves. Due to these challenges and increasing environmental worries, vegetable oils have become potential alternative solutions. These oils offer an environmentally sustainable solution for HTF applications because they are renewable, eco-friendly, and non-hazardous. The research explores the potential of vegetable oil mixtures in ternary fluid systems to improve CSP system performance through their advantageous thermal and environmental properties. The performance of CSP systems remains constrained by conventional HTFs that exhibit low thermal conductivity which limits efficient heat transfer. Enhancing thermal conductivity in HTFs stands as an essential research pursuit because it boosts energy transfer efficiency while simultaneously increasing energy output and reducing operating

costs. Optimized HTFs enable CSP technologies to compete better while facilitating the move to sustainable and cleaner energy solutions.

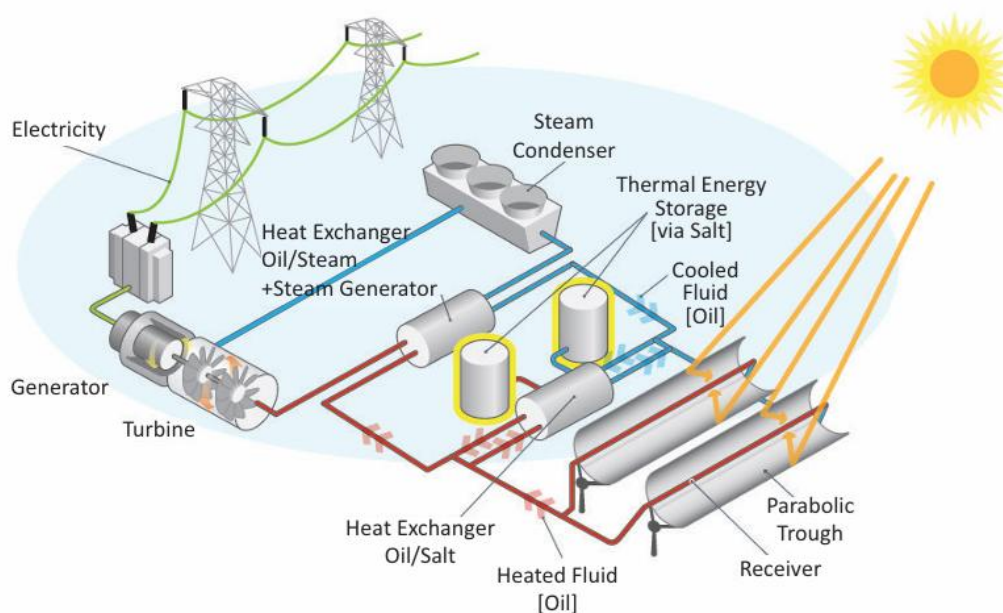


Figure 1: Schematic diagram of concentrated solar power [13]

2.0 Methodology

2.1. Materials and sample preparation

This research examines ternary Organic-Based thermal energy storage fluids which contain oregano oil (*Origanum vulgare*), olive oil (*Olea europaea*), and castor oil (*Ricinus communis*). The selected components demonstrated favorable thermophysical properties and local availability while offering low cost and high thermal stability which combined with the practical benefits of organic compounds led to a sustainable reduction in synthetic fluid use, making them suitable for thermal energy storage TES applications in concentrated solar power (CSP) plants. The organic-based fluids utilized in this study achieved high purity ($\geq 99\%$) and originated from established suppliers. The fluids were applied in their pure form to accurately represent standard industrial operating conditions.

2.1.1 Rationale for Weight Percentages

To enhance the thermal and oxidative stability of the mixture, a high percentage of oregano oil, ranging from 55% to 70%, was selected due to its rich antioxidant content primarily attributed to its high content of phenolic compounds, particularly carvacrol and thymol [22 - 24]. These elevated proportions are tested to maximize benefits, particularly in high-temperature applications. Additionally, moderate values of 20% to 40% were chosen for olive oil to balance thermal conductivity, heat capacity, and oxidation resistance. Olive contains oleic acid which contributes to its oxidation resistances [25]. Various proportions are tested to find the optimal balance between stability and thermal efficiency. Finally, a controlled proportion of castor oil, 10% to 15% was incorporated. Lower proportions ensure these benefits without adversely affecting the mixture's overall viscosity and handling properties.

Table 1 outlines the seven ternary mixtures to be investigated, each with different proportions of oregano oil, olive oil, and castor oil.

Table 1: Sample Matrix for the ternary blend mixture

Sample	Oregano oil %	Olive oil %	Castor oil %
SO1	60	30	10
SO2	50	40	10
SO3	70	20	10
SO4	60	25	15

SO5	65	25	10
SO6	55	35	10
SO7	57	28	15

2.1.2 Nanoparticle Doping

In this study, aluminum oxide (Al_2O_3) nanoparticles having 20-30 nm size and 99.9% purity were used as doping agents due to high thermal conductivity and for its ability to enhance the thermal conductivity of base fluids [26, 27]. A consistent doping concentration of 5 wt% Al_2O_3 was utilized, aligning with previous research [28] that indicated this concentration effectively improves thermal conductivity while keeping agglomeration effects low and stability in the oil matrix.

2.1.3 Mixing and homogenization

Each oil component was weighed on an analytical balance (Mettler Toledo XS205DU, 0.01 mg readability) with high precision, guaranteeing an accurate control of composition.

Dispersions were made so that nanoparticles would be optimally distributed in the ternary oil mixture. This involved firstly using an ultrasonicator (Qsonica Q700) to disperse Al_2O_3 particles in ethanol for 30 minutes. This helped break any agglomerates of particles and accordingly improve the uniformity of the nanoparticle suspension. Later, the ethanol suspension containing the nanoparticles was dried for 24 hours at 120°C with a vacuum pressure of 50 mbar in an Across International ADP-31 vacuum oven. This action was essential to preventing moisture from influencing thermal conductivity and thermal stability during characterization. Finally, the dried Al_2O_3 was added to the ternary oil mixture and subjected to ball milling for 60 minutes, ensuring uniform nanoparticle dispersion within the oil matrix. This careful preparation gave significant enhancements to the thermal properties and stability of the ternary oil mix.

2.2 Differential Scanning Calorimetry (DSC) Analysis

2.2.1 Instrumentation

A TA instrument 2920 MDSC V2.6A, modulated differential scanning calorimeter (MDSC) was used to carry out the thermal analysis. This instrument was selected due to its high sensitivity (0.2 μW), temperature reproducibility ($\pm 0.05^\circ\text{C}$), and temperature accuracy ($\pm 0.1^\circ\text{C}$), as specified by the manufacturer. These features, together with the accuracy in measuring heat flow and thermal events, make MDSC ideally suitable for the evaluation of thermal properties of ternary fluid systems.

2.2.2 Experimental/ Measurement Procedure

The thermal properties of the ternary fluid samples were measured using differential scanning calorimetry (DSC) following the configuration illustrated in the schematic diagram in Figure 2. This setup shows the arrangement of the sample and reference pans, thermoelectric disc, thermocouple junction, and gas purge inlet, which are critical for accurate heat flow measurements. The heat flow was calibrated using indium, and the heat capacity by means of a sapphire standard.

A 7.2000 mg sample of the ternary fluid was poured into an aluminum crucible (sample pan) covered with a lid and sealed with pressure using a crimper press. The sample pan has a cross-sectional area of 7.065 mm² and was filled with the ternary fluid to a height of 0.76 mm. The reference pan of identical type as the sample pan and of equal weight was left empty to serve as a baseline for comparison. The sample was heated at a ramp rate of **10°C/min**, held at **25°C (298 K) for 5 minutes** to allow the system to reach thermal equilibrium, ensuring uniform temperature throughout the sample and the crucible. This step minimizes thermal gradients that could affect the accuracy of subsequent measurements. After then the sample was heated from **25°C (298 K) to 87°C (360 K)** under a dynamic nitrogen atmosphere with a flow rate of **40 mL/min** to prevent oxidation. Data were collected in terms of heat flow (mW) and derivative heat flow (mW/K), both recorded as a function of temperature.

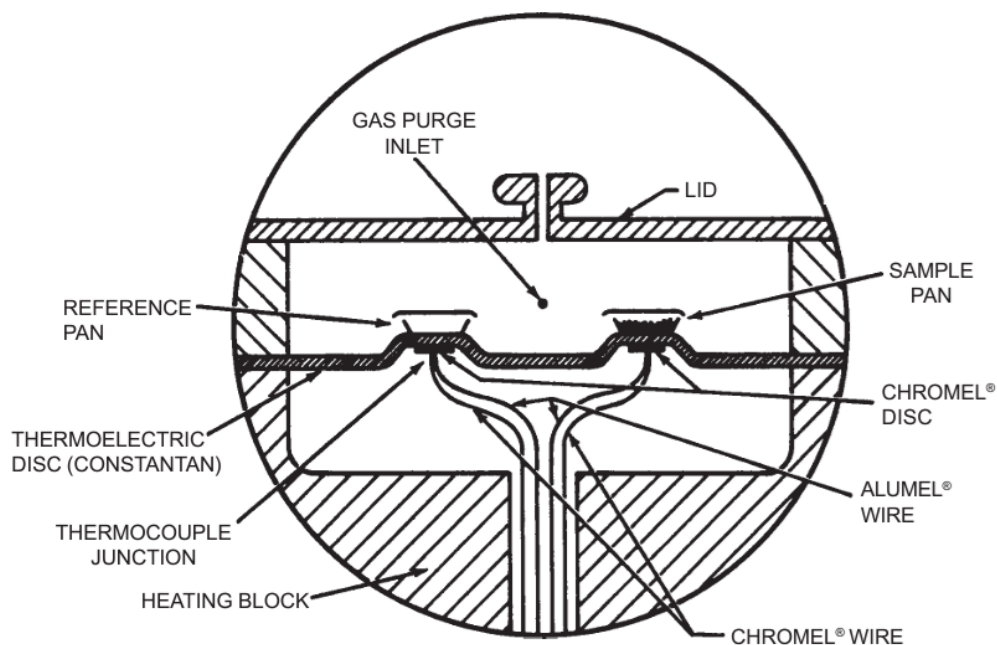


Figure 2. Schematic of Heat Flow Flux [29]

2.2.3 Thermal Conductivity Calculation

The set of equations 1 to 5 presented defines the relationship between thermal resistance, thermal conductivity, heat flow, and temperature change in the context of measuring thermal properties using Differential Scanning Calorimetry (DSC). Equation (6) relates thermal conductivity to the slope and physical properties of the sample. These equations enable precise calculations of thermal conductivity, an essential property for understanding heat transfer in ternary fluid. Equation (6) was used to compute the thermal conductivity (C).

$$\frac{1}{R_s} = \frac{\Delta Q}{\Delta T} \quad (1)$$

$$\frac{1}{R_s} = \frac{CA}{h} \quad (2)$$

$$\frac{\Delta Q}{\Delta T} = \frac{CA}{h} \quad (3)$$

$$S = \frac{\Delta Q}{\Delta T} \quad (4)$$

$$C = \frac{\Delta Q}{\Delta T} \frac{h}{A} \quad (5)$$

$$C = S \frac{h}{A} \quad (6)$$

Where:

C = Thermal conductivity ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)

$\Delta Q/\Delta T = S$ Measured slope from the DSC curve

Sample height, h = Constant (0.76 mm)

Surface Area occupied by the sample, A = Constant (7.065 mm^2)

2.3 Uncertainty Analysis

The uncertainty analysis of the reported thermal conductivity values for the ternary fluid system required the identification and quantification of various potential error sources to maintain accurate and reliable experimental results. Multiple factors influence the final uncertainty measurement. Weighing Uncertainty: The Mettler Toledo XS205DU analytical balance with 0.01 mg readability and an estimated uncertainty of ± 0.001 g was employed to measure weighing uncertainty in the ternary fluid mixture. The mass precision of individual fluid components may be compromised by this measurement uncertainty which in turn could alter the composition and thermal conductivity results. The balance underwent calibration using certified standard weights before the weighing session to correct any systematic errors and minimize measurement effects. The rigorous calibration process led to improved mass measurement accuracy which reduced weighing uncertainty effects on final thermal conductivity values.

Temperature uncertainty plays a significant role in the accuracy of thermal conductivity measurements, particularly in determining onset temperatures. The Differential Scanning Calorimeter (DSC) used in the experiments has a temperature accuracy of $\pm 0.1^\circ\text{C}$. This level of precision is crucial, as even small variations in temperature can influence the thermal conductivity calculations. These minor fluctuations affect the energy absorption and heat flow in the sample, which in turn impacts the determination of key thermal properties. Despite this precision, the temperature uncertainty still contributes to some variability in the results, which was carefully accounted for in the overall uncertainty analysis.

Heat flow uncertainty is an important factor in determining the precision of thermal conductivity measurements, as the DSC's heat flow measurements typically have an accuracy of $\pm 2\%$. This uncertainty directly affects the accuracy of the thermal conductivity calculations since heat flow is a critical parameter in these computations. Additionally, temperature variations, though minor, further propagate into the thermal conductivity results. To account for this, a detailed uncertainty analysis was conducted, where the uncertainty from the heat flow measurements was combined with other sources using the root-sum-square method. This approach ensured that the impact of heat flow uncertainty on the final thermal conductivity values was accurately quantified and minimized, improving the reliability of the reported data.

Sample preparation uncertainty arises from factors like incomplete mixing, inhomogeneity, and residual moisture content, which can introduce variability into the measurements. Although rigorous mixing and drying procedures were employed to minimize these issues, some residual uncertainty remains due to the potential for slight inconsistencies in sample composition or moisture retention. These factors were carefully considered in the overall uncertainty analysis to ensure accurate and reliable results.

The uncertainties from each source were individually quantified and then combined using statistical methods to determine the overall uncertainty in the reported thermal conductivity values. This combined standard uncertainty was calculated through the root-sum-square method, resulting in an expanded uncertainty reported with a coverage factor of 2, which corresponds to an approximate 95% confidence level.

$$U = KU_c \quad (8)$$

$$U_c = \sqrt{u_1^2 + u_2^2 + u_3^2 + \dots + u_n^2} \quad (9)$$

Where:

U is the expanded uncertainty, k is the coverage factor ($k = 2$ for 95% confidence level) and U_c is the combined standard uncertainty.

$u_1, u_2, u_3, \dots, u_n$ are the standard uncertainties from different sources.

The combined standard uncertainty (U_c) is calculated by combining the individual standard uncertainties from various sources using the root-sum-square method:

3. Results and discussion

3.1. Thermal conductivity of the Undoped Ternary Fluid

The thermal conductivity of the undoped ternary fluid samples, as shown in Table 2, varies across the different sample IDs. These values represent the heat transfer efficiency of each fluid without any dopant material. The thermal conductivity values of the undoped ternary fluid samples range from $0.2886 \text{ W/m}\cdot\text{K}$ to $0.5233 \text{ W/m}\cdot\text{K}$, with SO_2 demonstrating the highest value, suggesting that the composition of the ternary fluid plays a significant role in its ability to conduct heat efficiently.

Table 2 presents the thermal conductivity of both the undoped ternary fluid and the doped samples, showing various compositions variations across different sample IDs. This metric indicates each fluid's ability to transfer heat, with or without the added dopant. The measured thermal conductivity values range from 0.2886 W/m·K to 0.5233 W/m·K, with SO2 demonstrating the highest value, suggesting that the composition of the ternary fluid plays a significant role in its ability to conduct heat efficiently.

When compared to literature values for individual vegetable oils, the thermal conductivity of the undoped ternary fluids exhibits a notable enhancement. For instance, olive oil has been reported to have thermal conductivity values between 0.166–0.163 W/m·K at temperatures ranging from 20°C to 80°C [30]. Similarly, the average thermal conductivity of vegetable oils, including those similar to olive oil and castor oil, ranges from 0.167 W/m·K at 20°C to 0.137 W/m·K at 230°C [31]. Literature further indicates that castor oil exhibits a higher thermal conductivity, generally around 0.18 W/m·K [32; 33]. The observed range of 0.2886 W/m·K to 0.5233 W/m·K for the ternary mixture suggests a significant enhancement in thermal conductivity compared to individual oils. This improvement is likely attributed to synergistic molecular interactions among olive, castor, and oregano oils, which may facilitate more efficient heat transfer within the ternary system. These findings highlight the potential advantages of ternary fluid formulations in applications requiring enhanced thermal transport properties.

Table 2: Summary of Thermal Conductivity Measurements

Sample ID	Melting Point (K)	Thermal Conductivity (W/m·K)	Thermal Conductivity with 5% Al ₂ O ₃ (W/ m·K)	Percentage Change
SO1	334.39/335.68	0.3542	-	-
SO2	334.92/335.88	0.5233	0.3479	-33.5%
SO3	335.06/336.21	0.4144	-	-
SO4	334.55/335.99	0.2886	-	-
SO5	333.48/334.81	0.4633	0.4803	3.7%
SO6	334.08/335.45	0.4910	-	-
SO7	334.21/335.52	0.4928	0.4732	-4.0%

$$\text{Percentage Change} = \frac{(\text{Base Thermal Conductivity with Al}_2\text{O}_3 - \text{Base Thermal Conductivity}) \times 100}{\text{Base Thermal Conductivity}} \quad (7)$$

Samples SO1 to SO7 display varying thermal conductivities, directly influenced by their oil compositions, which is important for selecting a suitable heat transfer fluid (HTF) for concentrated solar power (CSP) systems. Among them, SO1 exhibits the lowest thermal conductivity at 0.3542 W/m·K, primarily due to its high proportion of oregano oil, which hinders heat transfer. Oregano oil is composed mainly of terpineol (E) Beta (55.5%), terpinen-4-ol (15.9%), and thymol (12.9%), compounds known for their weak intermolecular interactions and low thermal diffusivity, contributing to its poor thermal conductivity [34]. However, oregano as essential oil has low viscosity compare to olive oil and castor oil, its low viscosity enhances fluidity and pumpability, while its phenolic compounds improve oxidative stability by increasing resistance to degradation. Additionally, oregano oil's antimicrobial [35] properties may offer corrosion resistance by preventing microbial-induced corrosion in CSP systems. Despite these benefits, the presence of olive and castor oils; both of which have relatively low thermal conductivity and higher viscosity; further reduces heat transfer efficiency, making SO1 less suitable for CSP applications that require effective thermal conductivity.

In contrast, **SO2** demonstrates a significantly improved thermal conductivity of **0.5233 W/m·K**, attributed to a higher percentage of olive oil, which has better thermal conduction properties than oregano oil. Castor oil, known for its heat transfer capabilities, further enhances the thermal conductivity of the mixture. This optimized composition makes **SO2** more effective for heat conduction, making it well-suited for CSP systems. **SO3**, with a thermal conductivity of **0.4144 W/m·K**, strikes a balance in oil composition, providing moderate thermal conductivity while maintaining desirable properties such as viscosity and stability, ideal for CSP systems where a balanced thermal performance is required.

Samples SO6 and SO7 exhibit high thermal conductivities of 0.4910 W/m·K and 0.4928 W/m·K, respectively, due to their increased castor oil content. Castor oil enhances heat transfer by improving thermal conductivity while balancing viscosity mixture. Compared to olive oil, castor oil contributes to better heat conduction, while oregano oil, with its

lower viscosity, aids in fluidity but limits thermal conductivity. The minimal difference in thermal conductivity between SO6 and SO7 indicates that both formulations are highly efficient for applications requiring effective heat transfer, making them well-suited for CSP systems. On the other hand, **SO4** and **SO5**, with thermal conductivities of **0.2886 W/m·K** and **0.4633 W/m·K**, offer more moderate heat transfer capabilities. While **SO5** may serve as a balanced choice for moderate CSP applications, **SO4** is more suitable for scenarios where insulation or slower heat transfer is needed, rather than efficient heat conduction.

3.2 Factors Influencing Thermal Conductivity in Undoped Mixtures

Thermal conductivity in undoped mixtures, such as those composed of oils like oregano, olive, and castor oils, is influenced by several key factors that govern the flow of heat through the fluid. These factors include the composition and proportions of the constituent oils, viscosity, molecular interactions, and the physical properties of each individual component.

3.2.1. Composition and Proportions of Oils: The types and ratios of oils incorporated into the mixture are of primary importance in determining thermal conductivity. Vegetable oils like olive oil and castor oil generally have higher thermal conductivities compared to essential oils like oregano oil. For instance, studies have shown that the thermal conductivities of olive oil and castor oil are approximately 0.166 W/m·K [30] and 0.18 W/mK [33] respectively. For instance, an increased proportion of olive oil or castor oil in the mixture tends to enhance heat transfer, as these oils are known for their better heat conduction properties. In contrast, Higher concentrations of oregano oil, which have a lower thermal conductivity, reduce the overall ability of the mixture to conduct heat.

3.2.2. Viscosity of the Fluid: Heat transfer efficiency is deeply influenced by viscosity, with increasing viscosity of the ternary fluid has the tendency to reduce thermal conductivity of the mixture. In the ternary fluid system of oregano, olive, and castor oils, viscosity variations impact performance. Oregano oil has low viscosity but weak thermal conductivity as essential oil compare to vegetable oil such as olive oil and castor oil, while castor oil, with moderate viscosity, enhances heat transfer. Olive oil provides stability. This trend is consistent with previous research, as demonstrated by the sample SO5 (65% oregano, 25% olive, 10% castor), which had a 3.7% rise in the thermal conductivity with 5% Al_2O_3 , and SO7 (57% oregano, 28% olive, 15% castor) that had a 4.0% decrease, revealing that excessive viscosity hinders the proper nanoparticle dispersion[14]. These findings align with prior studies, reinforcing that optimizing viscosity is key to improving oil-based heat transfer fluids [36].

3.2.3. Molecular Interactions and Particle Dispersion: The effectiveness of thermal conductivity in a mixture also depends on how well the molecules of each oil interact with each other and how evenly the components are dispersed. Homogeneous mixtures with good molecular interactions between the oils tend to exhibit better heat transfer. Poor dispersion or phase separation can lead to inconsistencies in the heat conduction properties, as localized areas of higher or lower thermal conductivity may form, reducing the overall effectiveness.

3.2.4. Chemical Properties and Stability: The thermal conductivity of ternary fluid is also influenced by the chemical composition and stability of oil mixtures. For example, olive oil contains an oleuropein a major phenolic compound which acts as antioxidant [37] that help to maintain the thermal stability of the ternary mixture at higher temperatures contributing to the thermal properties by significantly inhibit thermal-induced peroxidation, thereby improving oil's quality and extending its shelf-life during thermal oxidation. The presence of compounds such as carvacrol in oregano oil may impact its ability to transfer heat effectively, while the high ricinoleic acid content in castor oil improves both its heat transfer properties and its resistance to freezing, further influencing the mixture's overall conductivity.

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3.3 Effect of Al_2O_3 Nanoparticle Dopant on Thermal Conductivity

The addition of 5% wt of Al_2O_3 nanoparticles as a dopant into the ternary fluid mixture has a significant effect on its thermal conductivity. The thermal conductivity of Al_2O_3 nanofluids increases with the concentration of nanoparticles, demonstrating a direct correlation between nanoparticle weight fraction and thermal performance [38, 39].

This effect can be understood through various mechanisms such as the nanoparticle's size, dispersion interaction with the fluid phases, and the formation of percolation networks. These modifications can either enhance or reduce the thermal conductivity of the fluid, depending on several factors.

3.3.1. Increase in Thermal Conductivity

The addition of Al_2O_3 nanoparticles in sample SO5 led to increase in thermal conductivity from $0.4633 \text{ W/m}\cdot\text{K}$ to $0.4803 \text{ W/m}\cdot\text{K}$, a 3.7% increase as shown in Table 2. At a concentration of 5% wt of Al_2O_3 , nanoparticle dispersion likely led to the formation of an effective network that improved thermal pathways by establishing thermal bridges between the fluid molecules, enhancing overall conductivity. Al_2O_3 nanoparticles, being highly conductive, further reduced thermal resistance and facilitated efficient heat conduction across the fluid. Additionally, these nanoparticles might have induced possible structural changes within the fluid, optimizing heat transfer properties through beneficial interfacial interactions.

3.3.2. Decrease in Thermal Conductivity

In contrast to sample SO5, samples SO2 and SO7 experienced a decrease in thermal conductivity upon the addition of 5% wt of 20 nm Al_2O_3 nanoparticles. For instance as shown Table 2, the thermal conductivity of SO2 dropped from $0.5233 \text{ W/m}\cdot\text{K}$ to $0.3479 \text{ W/m}\cdot\text{K}$, representing a 33.5% decrease. There are several reasons that could account for this reduction in thermal conductivity. First, agglomeration of nanoparticles at higher concentration levels leads to clumping of the particles, diminishing the effective heat-conducting pathways available in the fluid. This agglomeration disrupts the formation of the percolation network, leading to a decrease in overall thermal conductivity. Apart from this however, the presence of nanoparticles can cause an increase in the viscosity of the fluid thus hindering its capacity to flow and effectively transfer heat, hence diminishing thermal advantages brought about by the nanoparticles especially when the dispersion is poor. The nanoparticles on the other hand can also increase the interfacial resistance at the interfaces between the nanoparticles and the fluid and if the interactions are not optimized, this increases the thermal resistance and therefore reduces the efficiency of heat transfer leading to reduction in the thermal conductivity.

3.4. Agglomeration of Nanoparticles and Dispersion: Agglomeration or the clumping of nanoparticles reduces their dispersion in fluids, as observed in SO2 and SO7 in Table 2. This leads to photon scattering, weaker thermal bridges, and disrupted thermal pathways, all of which decrease thermal conductivity. Poor dispersion hinders heat transfer and reduces performance. In contrast, proper dispersion, as demonstrated in SO5, enhances thermal conductivity by 3.5%, creating an effective network that improves heat transfer and maximizes thermal performance.

3.5. Viscosity: In the case of SO2 and SO7, one of the adverse effects of adding nanoparticles is an increase in the viscosity of the fluid and hence, the resistance to flow. This increased viscosity reduces the ability of SO2 and SO7 to effectively transfer heat through convection, which may counter the benefits of enhanced thermal conductivity due to the addition of nanoparticles.

3.6. Local Structural Changes and Percolation Network Formation: The introduction of nanoparticles may lead to local structural changes in the fluid that either enhance or weaken heat transfer properties. Nanoparticles' agglomeration has lowered conductivity in both SO2 and SO7, but SO2 experiencing a more significant drop as agglomerated particles disrupted the percolation network and thermal pathways. While SO7 was also slightly lower in conductivity, it was not as severe, suggesting incomplete dispersion and partial agglomeration. On the other hand, there is a rather slight increase in thermal conductivity in SO5 implying that well dispersed nanoparticles can create an effective percolation network that increases heat transfer. This comparison shows that both SO2 and SO7 were limited by agglomeration but SO5 dispersion improves its thermal conductivity performance.

3.7. Influence of Nanoparticle Size and Concentration: The size and concentration of the nanoparticles are important influences that determine their dispersal, agglomeration and thermal conductivity. Smaller nanoparticles as observed in SO5, are easy to disperse as thermal bridges are easier to form facilitating heat power. On the contrary, higher concentration of nanoparticles as in SO2 and SO7 may cause agglomeration resulting to loss of heat transfer effectiveness due to breakdown of percolation network and increase in viscosity which reduce thermal conductivity.

3.8. Effective Network and Thermal Bridges: Nanoparticle network is necessary to effect perfect heat transfer. This structure is developed when nanoparticles are dispersed properly to create a connected structure which is capable of efficient thermal transfer. In SO5, the better dispersed nanoparticles created bigger thermal bridges which increased thermal conductivity by a considerable amount. In contrast, in SO2 and SO7 it has been noticed that some regions containing agglomerated nanoparticles did not allow such a smooth structure to be formed, resulting in lower thermal bridges and poor heat transfer efficiency. This suggests that the development of robust nanoparticle network will enhance thermal performance.

3.9. Implications for TES Applications in CSP Systems

Thermal Energy Storage (TES) is particularly important in Concentrated Solar Power (CSP) systems for storing the excess of thermal energy produced during the day for use in times of low solar radiation like night time or cloudy weather. TES systems rely on heat transfer fluids (HTFs) for efficiently absorbing, storing and releasing thermal energy. In this sense, there has been an increasing level of interest in the inclusion of nanoparticles such as Al_2O_3 in HTFs owing to their capabilities in enhancing thermal conductivity which is a key factor in energy transfer efficiency within the system. Such improvements in thermal conductivity mean better heat absorption as well as rapid heat release thus improving the efficiency of the CSP system.

Nonetheless, the use of Al_2O_3 nanoparticles or other similar nanoparticles into the HTFs also comes with trade-offs that are worth considering in TES applications.

3.10. Trade-offs Between Thermal Conductivity and Other Properties

The addition of nanoparticles like Al_2O_3 into a ternary fluid with the goal to enhance thermal conductivity should take into account the trade-offs between enhanced thermal conductivity and other critical properties of the fluid, such as viscosity, stability, cost, material compatibility and system design. Some of these trade-offs are discussed below:

- (a) **Stability and Dispersion:** The stability of nanoparticle dispersion in the HTF is another important factor. If nanoparticles tend to agglomerate (clump together), the effective surface area available for heat transfer is reduced, which diminishes the benefits of the added nanoparticles. Agglomeration can also lead to issues such as clogging or damage to system components. Achieving uniform dispersion is key to optimizing the benefits of nanoparticle doping, but it may require the use of stabilizers or surfactants, which can add complexity to the system and increase costs.
- (b) **Viscosity:** Improved thermal conductivity is often accompanied by an increase in viscosity. When nanoparticles are added to the fluid, the fluid's flow resistance may increase, which can negatively affect the pumpability and circulation of the HTF. This higher viscosity could require more energy to circulate the fluid, potentially reducing the overall efficiency of the TES system. This trade-off must be carefully managed to ensure that the fluid can still flow easily through the heat exchanger and piping system, which are crucial for effective heat transfer.
- (c) **Cost and Economic Feasibility:** The use of nanoparticles such as Al_2O_3 increases the cost of the fluid compared to standard heat transfer fluids. In TES applications, especially for large-scale CSP systems, the economic feasibility of using nanoparticle-doped fluids must be considered. While the improvement in thermal conductivity might lead to better energy efficiency, the increased cost of nanoparticles, stabilization agents, and potential for maintenance might offset the performance benefits in some cases. Cost-effectiveness is especially important in CSP systems, where the goal is to minimize operational costs while maximizing energy efficiency.
- (d) **Material Compatibility and System Design:** The addition of nanoparticles to HTFs can impact the material compatibility with system components, such as pipes, pumps, and heat exchangers. Nanoparticles may cause erosion or wear on system components, potentially increasing maintenance needs and operational downtime. The system must be designed to handle these nanoparticles without compromising component life. The design of the TES system must also be adapted to ensure that the nanoparticle-doped fluid can flow efficiently without clogging or damaging critical components.
- (e) **Thermal Resistance at Interfaces:** As nanoparticles interact with the base fluid, they create interfaces where thermal resistance can form. If these interfaces are not optimized (for example, through functionalization or coating of nanoparticles), the overall heat transfer efficiency can be reduced. Therefore, even though the addition of nanoparticles can improve thermal conductivity, interfacial resistance can negate some of those benefits. These interactions need to be carefully controlled to ensure that the nanoparticles are enhancing, not hindering, thermal transfer.

While doping heat transfer fluids with nanoparticles such as Al_2O_3 offers significant improvements in thermal conductivity, these benefits must be weighed against the potential trade-offs in terms of viscosity, dispersion stability, interfacial resistance, cost, and system compatibility. For TES applications in CSP systems, careful optimization of nanoparticle concentration and fluid formulation is required to balance these trade-offs and ensure that the overall performance of the TES system is enhanced. This balance is crucial for maximizing the long-term efficiency and economic viability of the system.

3.11 Raw Material Pricing

The raw material costs for these components were obtained from market prices before conversion to per-kilogram values. Oregano oil is \$489.00 for 3.59 kg [40], and olive oil is available at offer price of \$9.67 for 13.54 kg [41]. Castor oil is available at \$26.95 for 3.5 kg [42], and aluminum oxide (Al_2O_3) as dopant is priced at \$225.90 per kg [43]. The table below presents the unit cost per kilogram for each material.

Table 3: Unit Cost of Raw Materials

Material	Cost [\$/kg]
Oregano oil	136.21
Olive oil	0.71
Castor oil	7.70
Aluminum oxide (Al_2O_3) (Dopant)	225.90

This breakdown provides insight into the cost structure of the materials used in the formulation of the ternary oil blend with Al_2O_3 doping.

3.12 Cost-Performance Tradeoff Analysis

Table 4 Cost of Mixtures.

Sample	Oregano Oil (%)	Olive Oil (%)	Castor Oil (%)	Cost Undoped (\$/kg)	Cost Doped (\$/kg)
SO1	60	30	10	\$82.71	-
SO2	50	40	10	\$69.16	\$77.00
SO3	70	20	10	\$96.26	-
SO4	60	25	15	\$83.06	-
SO5	65	25	10	\$89.48	\$96.31
SO6	55	35	10	\$75.93	-
SO7	57	28	15	\$78.99	\$86.34

3.13 Cost-Performance Tradeoff Analysis

Cost-performance tradeoff analysis mainly targets the doped combinations, since doping plays a critical role to improve the thermal conductivity of oil mixtures as well as the oil mixtures used in high temperature solar power tower (CSP) applications. The goal is to determine which doped mixtures strike the best balance between cost and thermal conductivity, ensuring that the chosen mixtures provide optimal performance for Thermal Energy Storage (TES) systems, while maintaining economic viability.

The scatter plot as shown in Figure 3 visually describes the relationship between the cost per kg and the thermal conductivity of doped and undoped ternary oil blends. In this analysis, the goal is to determine the mixtures that offer the best trade off between cost and performance, a critical aspect to determine their economic feasibility in CSP applications. Trends in mixed-conformal patterns for each mixture on the x-axis are visualized for mixed undoped color blue and mixed doped color red. The y-axis represents the thermal conductivity, which is considered the most important performance parameter of TES mixtures.

From Table 3 and Table 4, the doped mixtures show a modest price increase compared to their undoped versions, with costs ranging from \$77.00/kg (SO2 doped) to \$96.31/kg (SO5 doped). Although doping is generally associated with a small increase in cost, the improved thermal conductivity of the dopant mixture often compensates for this increase, so these doped mixtures are also viable for CSP applications with the requirement of high thermal conductivity to achieve high heat transfer and energy storage efficiency.

SO2 is one of the cheapest doped compositions with a marginal price increase from \$69.16/kg (undoped) to \$77.00/kg (doped). Nevertheless, doping leads to a 33.5% reduction in the thermal conductivity from 0.5233 W/m·K to 0.3479

W/m·K (indicated). Although the conductivity decreased, the slightly higher price still makes SO2 promising for a number of applications in which a lower thermal conductivity can be tolerated or cost reduction is paramount.

SO7, containing a doped price of \$86.34/kg, demonstrates a small reduction in thermal conductivity from 0.4928 W/m·K to 0.4732 W/m·K (4.0% lower), which makes its thermal conductivity more efficient. Although there is a slight performance decrease for example, a small price increase over the undoped version (\$78.99/kg) and a small change in conductivity, SO7 is a strong candidate for CSP applications. This blend provides a reasonable tradeoff between cost and conductivity, and thus is an attractive choice for applications where trustworthy operation can be achieved at relatively low cost.

SO5 is different in that it shows a 3.7% increase in thermal conductivity (from 0.4633 W/m·K to 0.4803 W/m·K) after doping. The doped is \$96.31/kg, a clear difference compared with the \$89.48/kg of the undoped material. Nevertheless, owing to a relatively small increase in conductivity and a relatively low increase in cost, SO5 constitutes an acceptable alternative for situations in which slightly improved conductivity is required but it without an excessive increase of cost. (SO1: \$82.71/kg, SO3: \$96.26/kg) although they have lower thermal conductivity values, they are not well suited for high-performance CSP applications. The undoped forms may not be ideal in accommodating the stringent thermal conductivity requirements in efficient energy storage and transfer based on TES systems.

The **doped mixtures**, on the other hand, provide a clear advantage in terms of enhancing thermal conductivity, despite the slight increase in cost. **SO2** and **SO7** offer the best balance of cost and performance, with **SO7** showing a minor reduction in conductivity that remains competitive for CSP applications. **SO5** offers a slight conductivity boost, and while **SO3** remains uncertain due to the lack of doping data, it is likely not the best choice given its high base cost.

Ultimately, the doping process provides a performance enhancement that justifies the minor increase in cost, especially for CSP applications that require high thermal conductivity for effective heat storage and transfer. The decision on which mixture to use will depend on the specific thermal conductivity needs and the allowable cost increase for CSP systems, with doped mixtures generally offering the best tradeoff between performance and affordability.

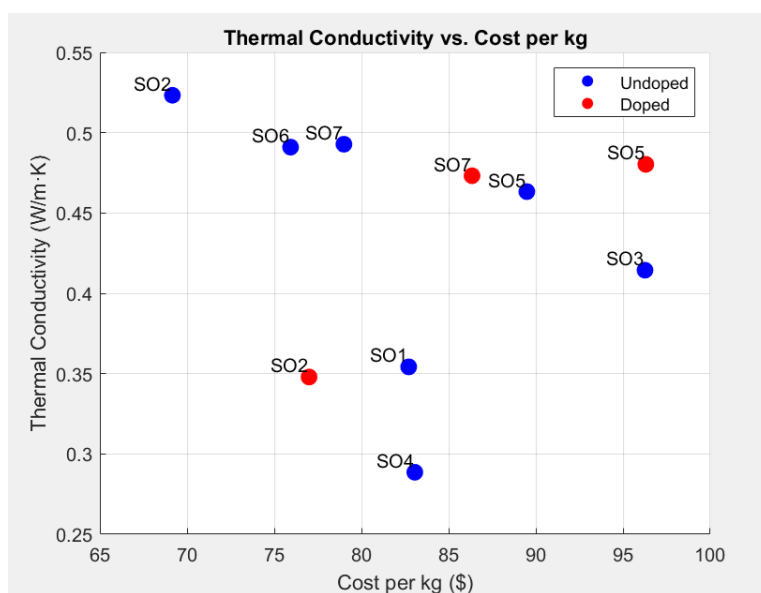


Figure 3: Plot of Thermal Conductivity (W/mK) against Cost per kg(\$)

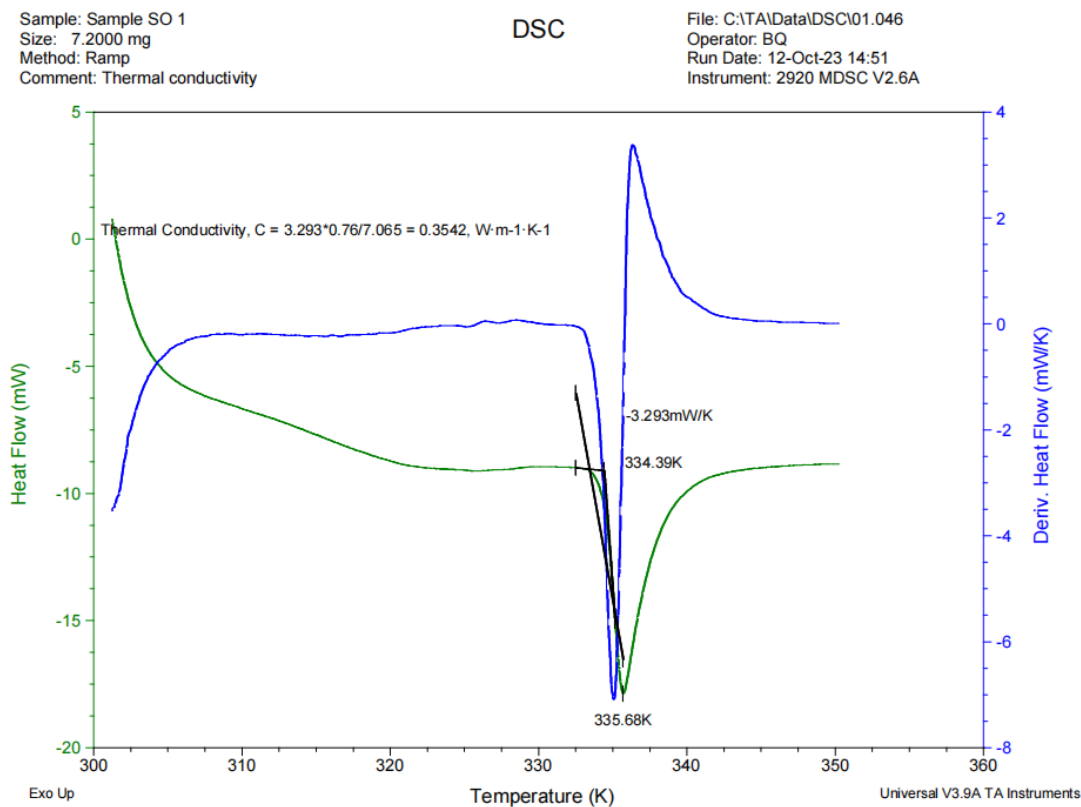


Fig. 1. Thermal conductivity of SO 1.

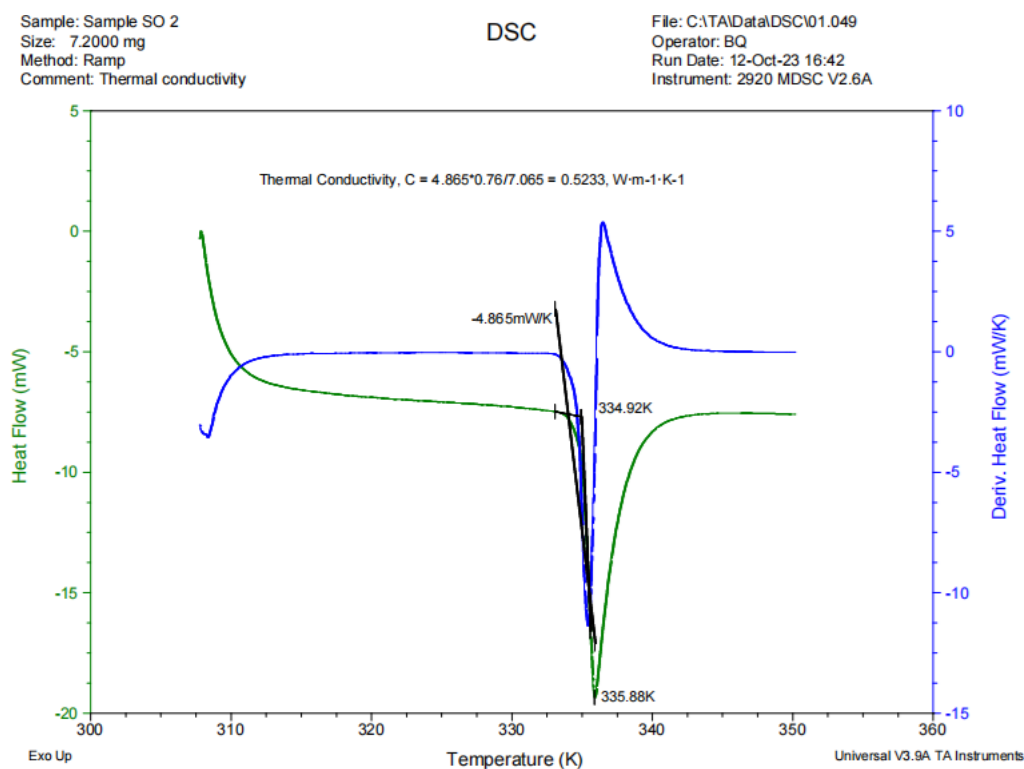


Fig. 2. Thermal conductivity of SO 2

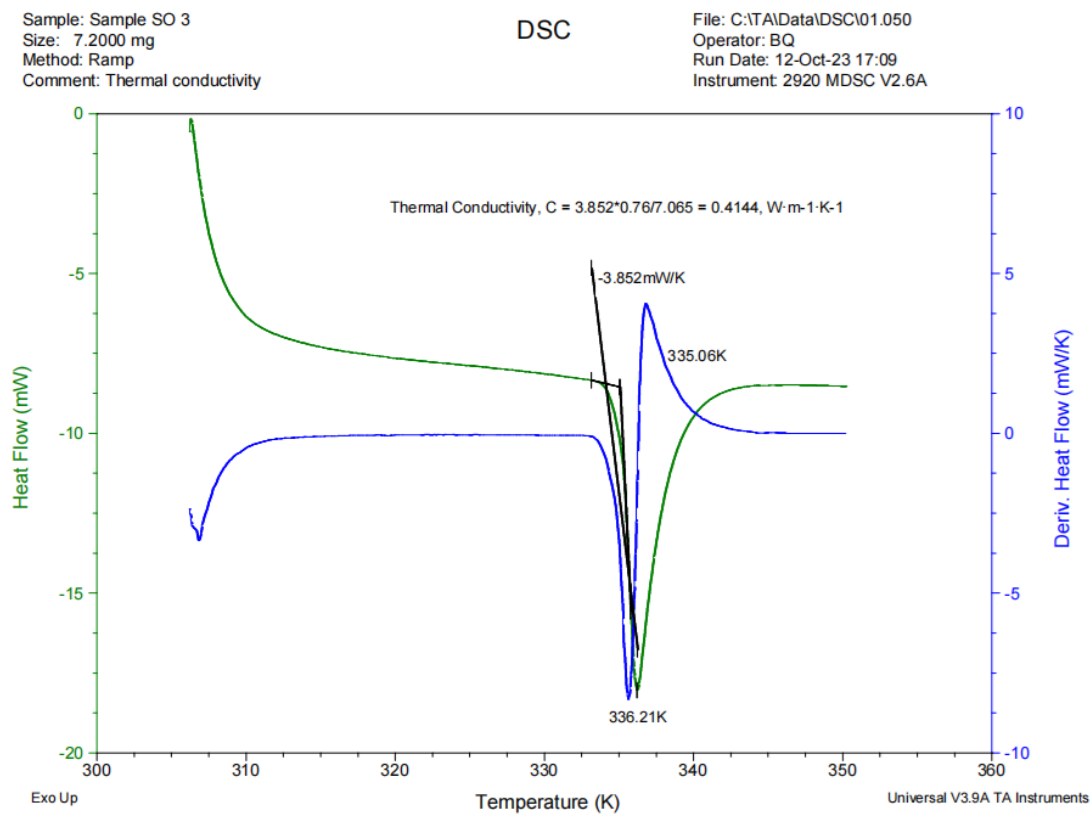


Fig. 3. Thermal conductivity of SO 3.

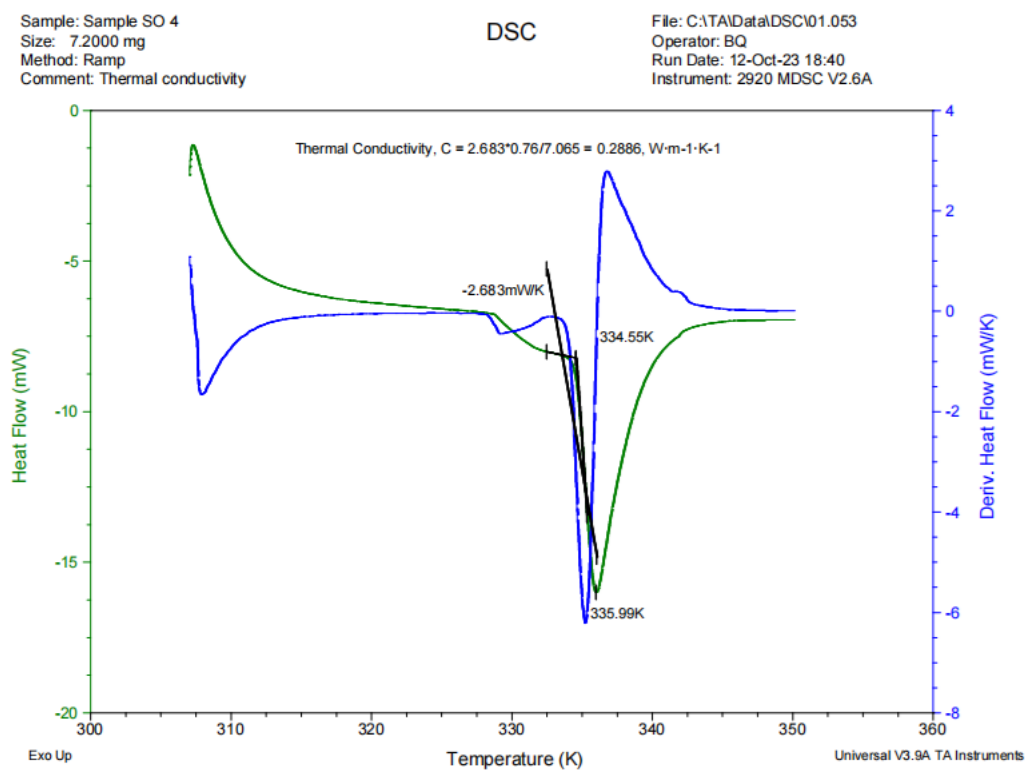


Fig. 4. Thermal conductivity of SO 4

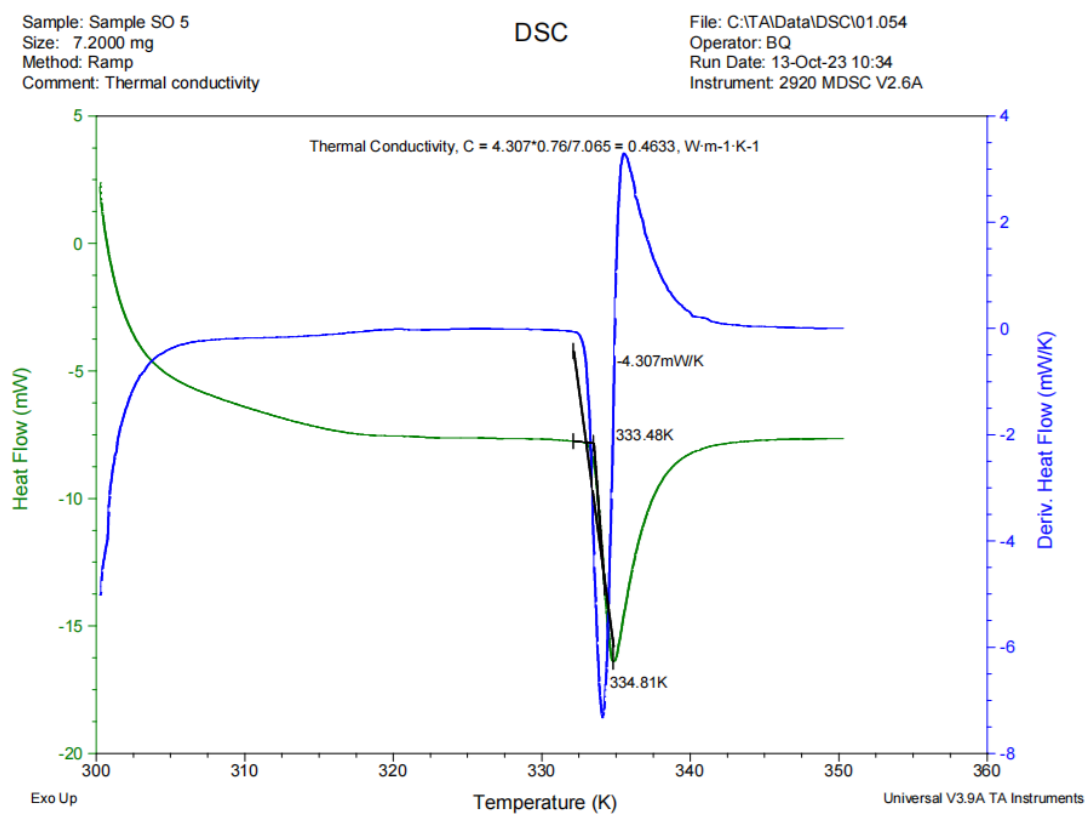


Fig. 5. Thermal conductivity of SO 5.

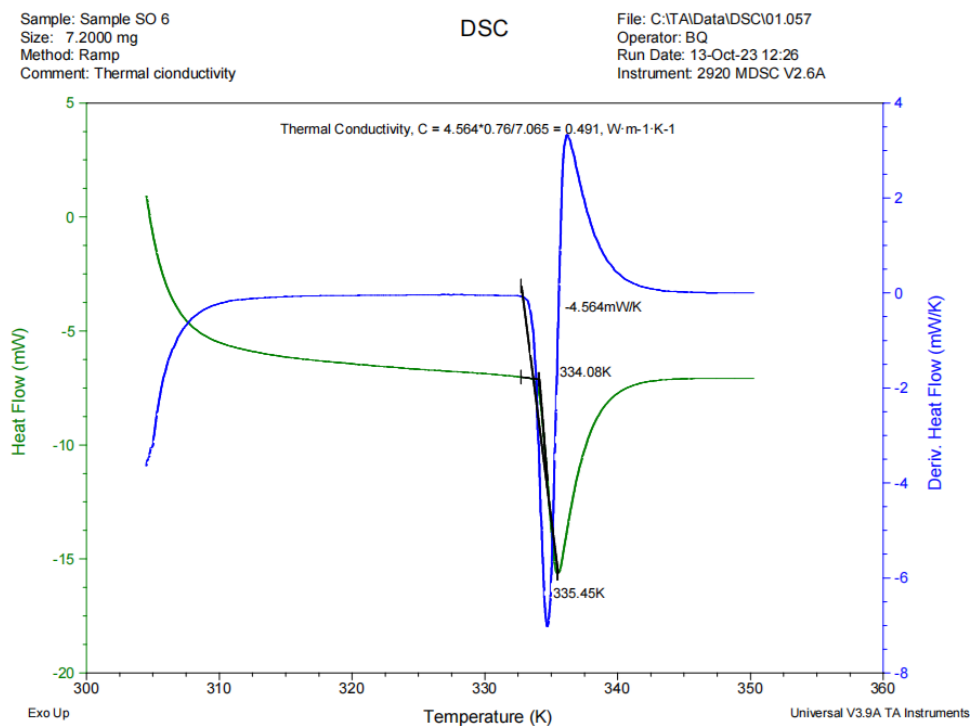


Fig. 6. Thermal conductivity of SO 6

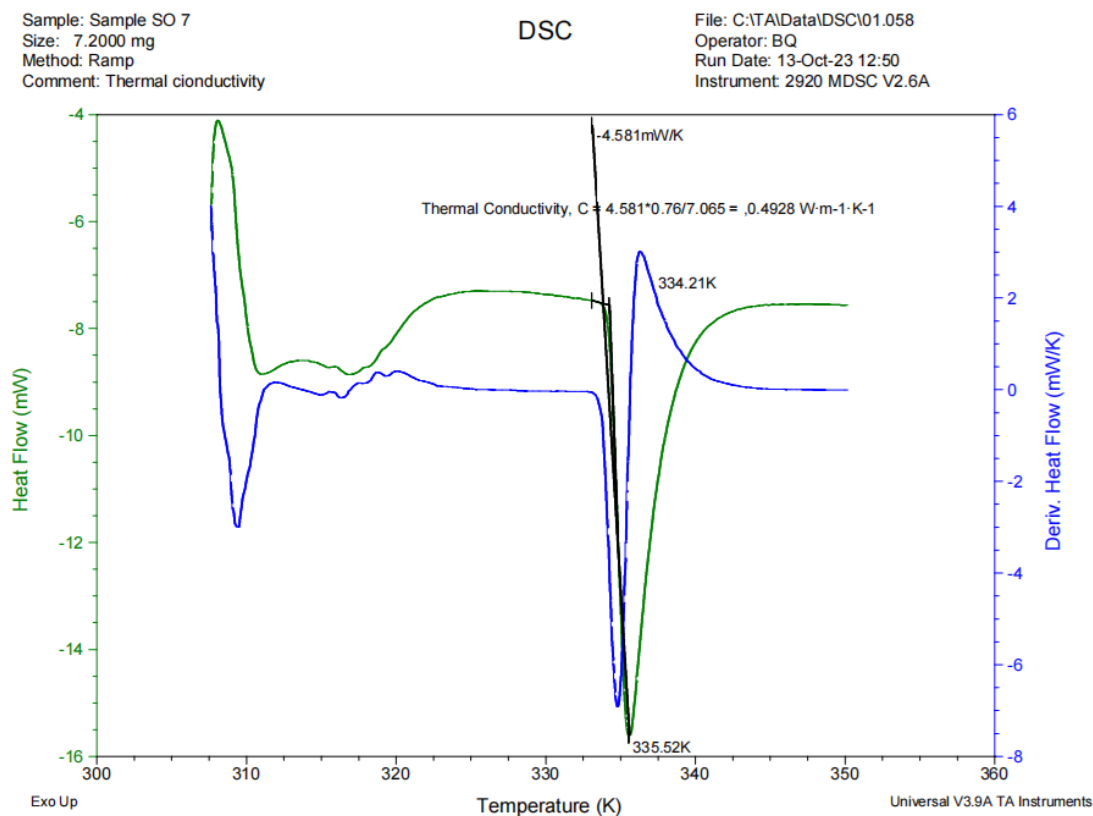


Fig. 7. Thermal conductivity of SO 7.

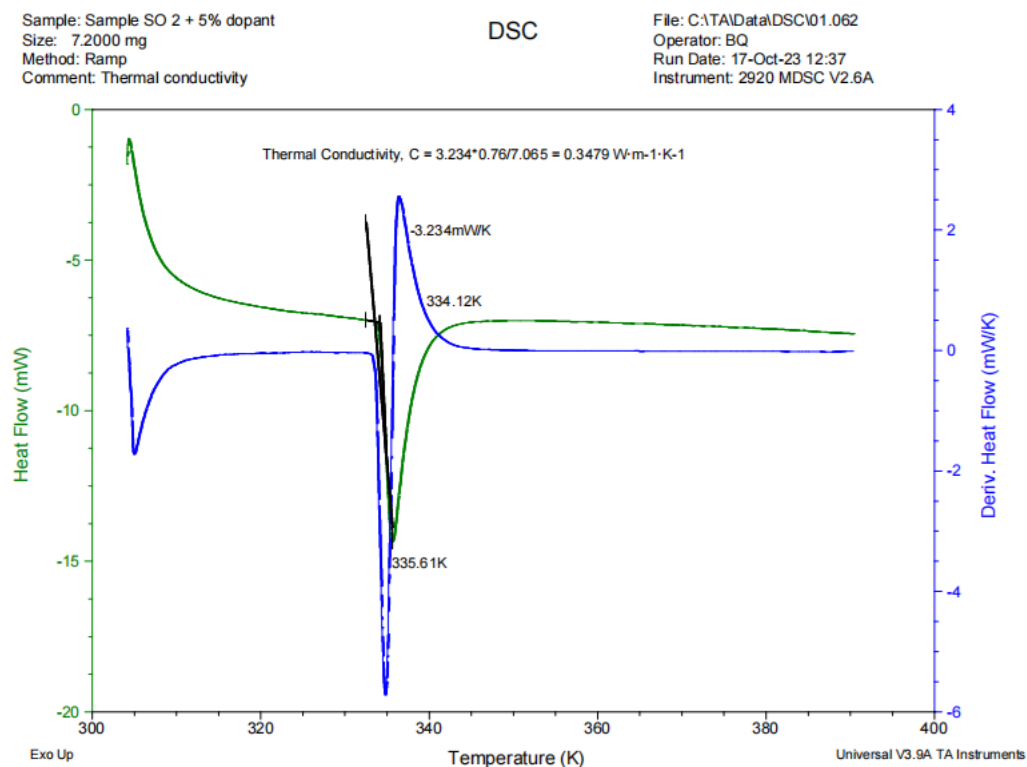


Fig. 8. Thermal conductivity of SO 2+5% Aluminum oxide nano particle

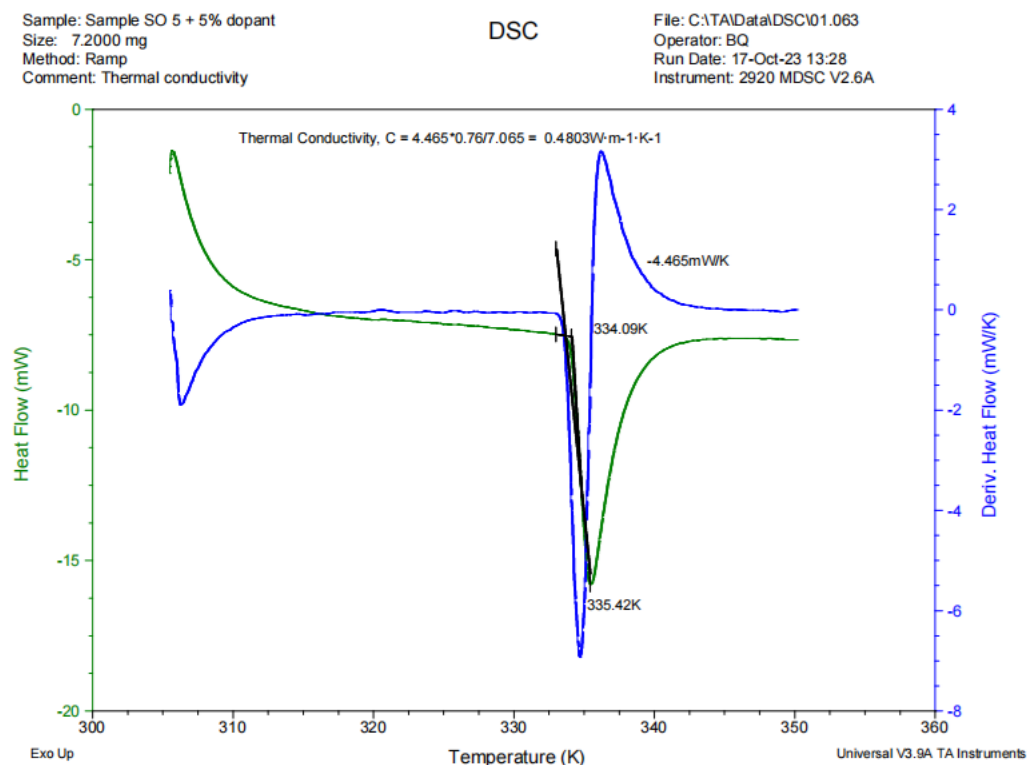


Fig. 9. Thermal conductivity of SO 5+5% Aluminum oxide nano particle

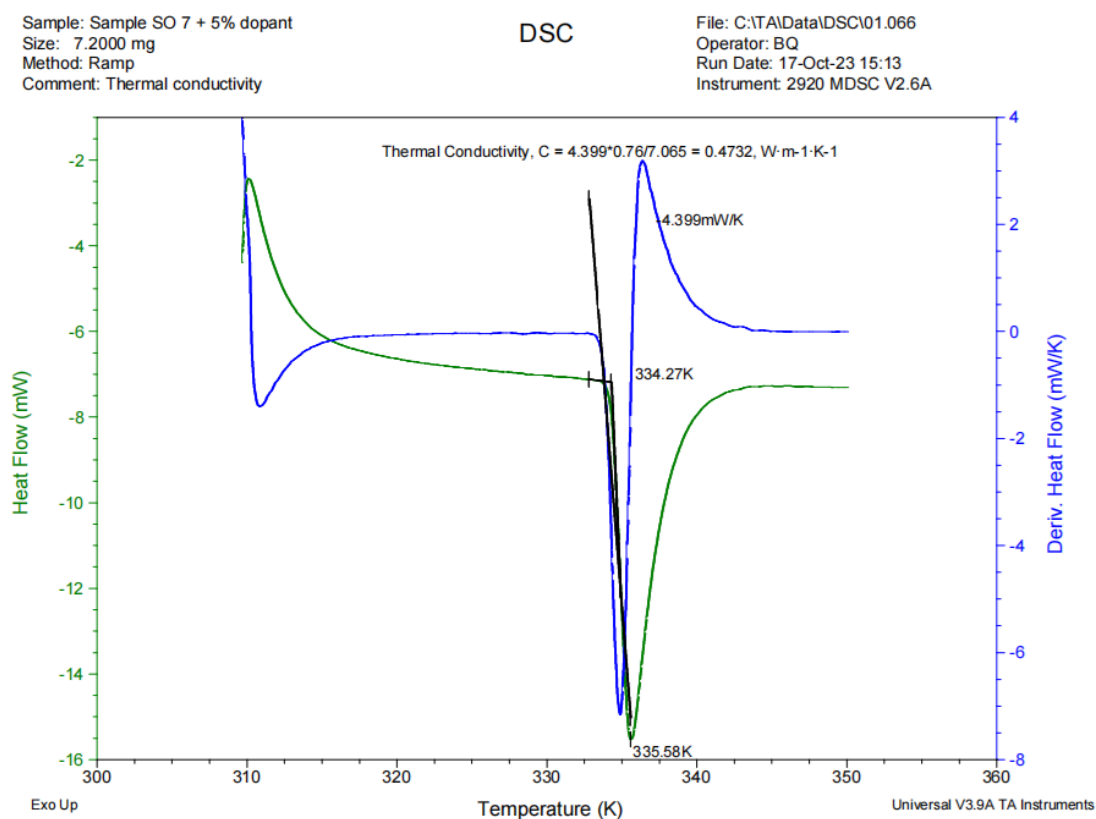


Fig. 10. Thermal conductivity of SO 7+5% Aluminum oxide nano particle

4.0 Conclusion and Recommendations

4.1 Conclusion

This study investigated the effect of 5% Al_2O_3 nanoparticle doping on the thermal conductivity and melting points of ternary fluid mixtures composed of oregano oil, olive oil, and castor oil in varying proportions. The key findings are as follows:

1. All ternary fluid samples exhibited melting points within a narrow range of 333.48 K to 336.21 K, confirming their thermal stability and suitability for thermal energy storage (TES) applications.
2. Among the undoped samples, SO2 displayed the highest thermal conductivity (0.5233 W/m·K), while SO4 had the lowest (0.2886 W/m·K).
3. SO5 experienced a 3.7% increase in thermal conductivity, improving from 0.4633 W/m·K to 0.4803 W/m·K, indicating a positive impact of nanoparticle doping.
4. In contrast, SO2 and SO7 showed significant reductions in thermal conductivity, with decreases of 33.5% and 4.0%, respectively.
5. Samples with higher oregano oil content (e.g., SO5, 65%) responded positively to Al_2O_3 doping, showing modest improvements in thermal conductivity.
6. Samples with higher olive oil content (e.g., SO2, 40%) demonstrated a substantial decrease in performance, suggesting potential incompatibility between olive oil and Al_2O_3 nanoparticles in the mixture.

4.2 Recommendations

1. **Optimize Ternary Oil Ratios:** SO5, with a composition of 65% oregano oil, 25% olive oil, and 10% castor oil, showed the best performance after doping. It should be used as a benchmark for further optimization of oil ratios. Future formulations should explore increasing oregano oil content while maintaining castor oil at moderate levels to improve thermal conductivity enhancements with nanoparticle doping.

2. **Reduce Olive Oil Content:** High olive oil content, as in SO2 (40%), appears to have negative affect the interaction with Al_2O_3 nanoparticles. Reducing the olive oil percentage may mitigate this issue and improve compatibility with nanoparticles.

3. **Investigate Alternative Nanoparticles:** To overcome variability in thermal conductivity responses, other nanoparticle types (e.g., SiO_2 or TiO_2) should be investigated for doping ternary fluid mixtures, as they may provide more consistent improvements.

1. **Prioritize SO5 for TES Applications:** With its favorable thermal conductivity and positive response to Al_2O_3 doping, SO5 is a promising candidate for TES applications and should be prioritized for further study and potential use in thermal energy storage systems.

5. **Further Analytical Studies:** Conduct additional thermal and structural analyses to better understand the interactions between Al_2O_3 nanoparticles and the ternary fluid components. This could help refine the formulation for enhanced TES performance.

These findings contribute to the development of advanced TES materials by providing insights into the complex interplay between ternary fluid composition and nanoparticle doping, paving the way for improved efficiency in energy storage systems.

Conflict of Interest

The authors declare no conflict of interest.

Author contribution statement

Leo Eromina Obogai: Investigation, Data Curation, Methodology, Formal Analysis, Writing Original Draft
Collins Chike Kwasi-Effah: Project Administration, Conceptualization, Methodology, Investigation
Henry Okechukwu Egware: Validation, Visualization, Writing - Review & Editing

Declaration of Competing Interest

The authors declare that they have no financial interests or personal relationships that could have influenced the work presented in this paper.

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