

Parametric evaluation of sensible heat storage systems using nano-ionic liquids

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ABSTRACT

The performance of nano-ionic liquids as working fluids for solar thermal energy storage systems is analyzed and compared to that of traditional water-based solar storage systems. Critical variables are evaluated via the experimental setup (e.g., heat capacity, collector instantaneous efficiency, and average tank temperature) to obtain the optimum nanoparticle concentration for maximum thermal performance. Results show a significant enhancement in the heat capacity of the ionic liquid 1-Butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF₆] with the addition of copper oxide nanoparticles (CuO). The best thermal performance is achieved with a 0.60% concentration of nanoparticles that provides a heat capacity increment of 34%. In addition, the instantaneous efficiency of the solar collector increased with the addition of nanoparticles to a peak efficiency of 74.17% at the 0.60% concentration. Moreover, the liquid phase temperature range of [Bmim][PF₆] with CuO nanoparticles is significantly more expansive than that of water. It remains a liquid up to 200 °C, compared to water at 100 °C. This broader temperature range makes it highly suitable for high-temperature applications without the water phase change limitations. However, it's important to note that higher concentrations of nanoparticles can lead to aggregation and reduced thermal performance. In conclusion, our study underscores the potential of nano ionic liquids, with optimized nanoparticle concentrations, as a convincing alternative to conventional thermal storage media. They offer clear advantages in high-temperature applications and can significantly enhance the overall efficiency of solar collector systems.

Keywords: ionic liquid, nanoparticles, storage capacity, thermal energy storage, and nano-ionic liquid.

INTRODUCTION

Thermal energy storage (TES) systems are crucial for storing solar energy, as they allow it to be stored for use during periods of low or no sunlight. This study optimizes sensible heat storage (SHS) systems in concentrated solar power (CSP) applications by mixing ionic liquids with nanoparticles to improve their thermal performance. Ionic liquids have a broad liquid-phase temperature range and significant heat storage capacity, making them ideal candidates for TES. When these liquids are enhanced with nanoparticles, their

thermophysical properties improve, such as thermal conductivity and heat capacity.

The growing interest in developing more efficient fluids for thermal energy applications has driven a rise in studies focused on fluids with improved thermophysical properties. In recent years, ionanocolloids – nanofluids based on ionic liquids – have attracted significant attention. These fluids combine the exceptional physicochemical properties of ionic liquids with enhanced thermal conductivity, thanks to the inclusion of nanoparticles that efficiently transfer heat. Moreover, their negligible vapor pressure

makes them environmentally friendly, offering a sustainable alternative for thermal management and energy-related applications.

Ionic liquids (ILs) are known for their high thermal stability, often capable of withstanding temperatures exceeding 200 °C, and in some cases, even up to 400 °C or higher. This makes them suitable for high-temperature energy storage applications, such as in CSP plants. In addition, high specific heat capacity in applications such as thermal energy storage systems allows ILs to store more thermal energy without requiring a large volume. Although ILs have moderate to high specific heat capacities, these are generally lower than water ones. Their composition determines their specific heat capacity, usually between 1 and 2 J/g·K. The base fluid, ionic liquid, may form nano ionic liquid to overcome this low specific heat capacity challenge [Kanti et al., 2022].

Research Studies were performed to study the impacts of nanoparticle incorporation on the thermal and physical properties of the ionic liquids.

Bridges et al. [2011] demonstrated ionic liquids supplemented with Al₂O₃ nanoparticles as potential thermal transfer fluids for CSP systems. Results indicated an almost 30% increase (and more than 40% for volumetric heat capacity) compared to conventional heat transfer fluids. After assessing the heat capacity at various temperatures, the nanoparticle-enhanced ionic liquids (NEILs) enhanced the CSP system efficiency. Additionally, long thermal stability tests showed that NEILs can be used for a long time in CSP and, hence, can make it possible to produce more solar power.

Paul et al. [2017] evaluated the potential of NEILs as heat transfer fluids for CSP systems, focusing on their thermal properties. NEILs, formed by dispersing nanoparticles into base ionic liquids (ILs), showed promising results. Experimental findings revealed that NEILs improved heat capacity by approximately 23% and thermal conductivity by about 6% compared to the base ILs, making them strong candidates for CSP applications to boost energy efficiency and lower operational costs. Additionally, NEILs demonstrated around a 20% increase in the heat transfer coefficient, further validating their effectiveness. These results suggest that incorporating NEILs into CSP systems is both practical and beneficial, potentially supporting the development of more cost-efficient and high-performance CSP technologies.

The amount to which ionic liquids (1-alkyl-3-methylimidazolium, butyl, hexyl, octyl, and

decyl) can be used for TES is presented in the study conducted by Bendová et al. [2019]. Advanced experimental techniques and mathematical statistics were employed to thoroughly analyze the energy density and heat capacity of these ionic liquids. It was concluded that these ionic liquids possess favorable characteristics, with their volumetric heat capacity and energy density falling in the range desired for SHS applications.

Aravind et al. [2021] examined the thermal behavior of an imidazole-based ionic liquid by incorporating two types of nanoparticles, copper and phosphate, designated as A and B. The properties of these mixtures were analyzed using various analytical techniques. The Specific heat capacities of the mixtures were determined to be 11 J/g·K for combination A and 2.8 J/g·K for combination B while using differential Scanning Calorimetry. Furthermore, the Specific heat capacity (C) was more significant for combination A than lead, tin, stainless steel, and aluminum at the point they melt (C=2.54 J/g·K), making this material a potential heat carrier. At particular temperatures, the two combinations also shifted from hydrated to dehydrated phases. For both combinations, we calculated the average sizes of crystals and found that the combinations suit various applications, including TES.

Main et al. [2021] conducted an experimental study to evaluate how nanoparticle size influences nanofluids' density, viscosity, and thermal conductivity based on ionic liquids (ILs). It was revealed that IL-based nanofluids have a higher density than the base ILs. However, there was no noticeable difference in density as a function of nanoparticle size. The viscosity of IL-based nanofluids did not show a significant difference in the size of the nanoparticles; one wt% of IL-based nanofluids exhibited an average ~ 13.71% viscosity improvement. However, for the one wt% IL-based nanofluids, 10 nm nanoparticles showed a maximum of 9.73% enhancement in effective thermal conductivity. Based on nanoparticle concentration, the viscosity and thermal conductivity of IL-based nanofluids containing 10 nm nanoparticles showed maximum enhancements of 30% and 11%, respectively, at a concentration of 2 wt%.

Das et al. [2021] conducted a comprehensive review on the use of ionic liquids and nanofluids in solar systems, emphasizing the role of advanced nanomaterials in achieving desirable properties. The study evaluates key attributes such as energy storage capacity (both sensible and latent), optical

properties (absorbance, transmittance, and molar extinction coefficient), thermal stability, conductivity, and viscosity. It also examines how variations in anions and cations influence these properties. The review provides a critical analysis of the applications of ionic liquids and nanofluids in various solar systems, highlighting recent advancements in nanoparticle integration. Notably, the review identifies nanofluids' superior sensible energy storage capabilities and their enhanced thermophysical properties. Additionally, it discusses the challenges that must be addressed for the practical implementation of these technologies.

Piper et al. [2022] discussed the evolution and promise of the emerging field of ionic liquids for renewable thermal energy storage. Systems are considered from a holistic, sustainable point of view, demonstrating the importance of assessing material origins and synthetic pathways and system performance through lifecycle assessment. We elucidate the emerging design rules for optimizing thermal properties and, in doing so, attempt to provide an overview of promising emerging systems and future directions.

Cavieres et al. [2022] elaborated on INFs, which are composed of two equimolar mixtures of ILs, as base fluids and Multiwalled Carbon Nanotubes (MWCNTs) with weight percentages of 0.04, 0.06, 0.08, and 0.1 wt%. Furthermore, the thermophysical properties of the proposed new materials were evaluated and compared to conventional materials currently used in solar energy storage systems. It was shown that the heat capacity (C_p) reaches increases of up to 3.7 and 3.2 times that of nitrated salts and commercial fluid, which translates into a 9.4% and 284% higher thermal storage density (E), respectively, and even lower thermal diffusivity (α), which supports the preliminary idea of using these new materials for energy storage.

Singh et al. [2022] reviewed recent advancements in INF systems and their applications in energy-related fields. They explored the synthesis of INFs using various nanoparticles (NPs) and analysed their thermophysical properties. The study also emphasized mathematical models for predicting thermal conductivity and viscosity. The selection of appropriate ionic liquids (ILs) and NPs is critical for optimizing heat transfer and storage applications, given their temperature-dependent physicochemical properties. Mathematical modeling offers a practical approach to identifying efficient heat transfer fluids, reducing

the need for extensive experimentation. The challenges and potential benefits of using INFs for heat transfer were also discussed.

Kanti et al. [2022] investigated the thermo-physical behaviour of the ionic liquid 1-ethyl-3-methylimidazolium chloride ([EMiM]Cl) mixed with Al_2O_3 nanoparticles over a temperature range of 303.15–333.15 K. Their findings indicated that both specific heat and thermal conductivity increase with rising temperature and concentration. In contrast, viscosity and density increase with concentration but decrease as temperature rises. The study proposed correlations for predicting specific heat, thermal conductivity, and viscosity based on the experimental data. Additionally, the heat transfer performance of the INF was theoretically assessed using the measured thermophysical properties.

The latest investigations about the utilization of ionic liquid nanofluids as a heat transfer fluid are summarized by Lingala [2023]. These summaries are broken down into three types: (a) the thermophysical parameters, including thermal conductivity, viscosity, density, and specific heat of ionic liquids (base fluids); (b) the thermophysical properties like thermal conductivity, viscosity, density, and viscosity of ionic liquids based nanofluids (IL nanofluids), and (iii) utilization of IL nanofluids as a heat transfer fluid in the thermal devices. The techniques for measuring the thermophysical characteristics and the synthesis of IL nanofluids are also covered. The suggestions for potential future research directions for IL nanofluids are summarized.

Sustainable INFs by Duarte et al. [2024] comprise dispersed Bombyx mori silk fibroin (SF) derived carbon dots in a bilayer solution of 1-butyl-3-methylimidazolium chloride (IL₁) and 1-(4-sulfonyl)-3-methylimidazolium triflate (IL₂). The thermal conductivity and heat capacity of the INFs are relatively high compared to current state-of-the-art INFs. However, the INFs can convert light to heat under suitable illumination conditions with up to 28% photothermal conversion efficiencies, comparable to other reported INFs. The range of working temperatures, SFIL₁IL₂ – 5h has marked stability.

In Al-Amayreh and Alahmaher [2024], phase change materials PCM and 1% Al_2O_3 nanoparticles were utilized to enhance thermal energy storage (TES) reliability in providing the heat supply during low solar radiation. A double-cylindrical shell with petroleum jelly and wax was used as PCMs, and a redesigned heat exchanger for better

efficiency was employed. Temperature profiles during charging and discharging are investigated in open and closed systems. A peak efficiency of 73% was achieved using the dual PCM system with nanoparticles, and the nanoparticles alone increased efficiency by 5%. The results demonstrated that dual PCM layers and nanoparticle additives could be utilized to enhance the efficiency of TES.

This study aims to improve solar thermal storage systems by utilizing nanoparticle-enhanced ionic liquids as working fluids. A series of experiments are conducted to assess the impact of nanoparticle concentration on key parameters, including heat capacity, collector efficiency, and storage tank temperature. The findings are compared with conventional water-based systems to highlight the potential benefits of these advanced materials. The conclusions and recommendations are a foundation for further advancements in solar thermal energy systems and other renewable energy technologies.

MATERIALS AND METHODS

This study developed an experimental setup that used a solar thermal energy simulator equipped with a fully functional model of a solar thermal system to investigate critical factors, including heat capacity, system efficiency, and tank temperature, that impact solar thermal domestic water heating.

Selection of materials

Copper oxide (CuO) nanoparticles are often used for PV cooling because of their unique

properties and advantages. Due to their significant characteristics, like high thermal conductivity, substantial surface area, stability, compatibility, cost-effectiveness, and ease of integration, these nanoparticles are extensively used in PV cooling applications. CuO nanoparticles are prevalent in PV cooling due to their high heat dissipation capability and essential role in maintaining PV systems' efficacy and durability. The CuO nanofluids with approximately 30 nm particles were purchased from US Research Nanomaterials Inc., Houston, TX, USA, and the ionic liquid 1-Butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF₆] was purchased from Haihang Industry Co., Ltd, China.

Test method

The experimental arrangement used in this study is shown in Figure 1. The primary apparatus employed is the ET 202: Principles of Solar Thermal Energy from Gunt, Hamburg. Twenty-five halogen lamps are mounted on the lighting unit (1). As an exception, halogen lamps are sometimes applied in scientific and industrial applications. While they do not replace real solar radiation, they were used in this study because it is difficult to reproduce all the possible light intensity spectrum and exposure duration parameters with natural sunlight.

Furthermore, a halogen lamp offers a better and more reproducible light source, which allows researchers to perform experiments under stable and predetermined conditions. The flat plate collector (2) is then illuminated, which causes the absorber to heat up. The flat plate collector

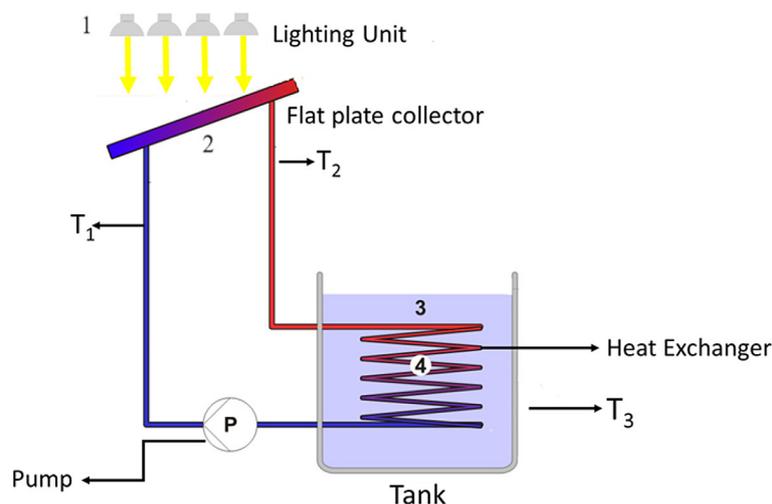


Figure 1. Experimental setup

section consists of the absorber that transfers heat to the circulating heat transfer fluid, which exits the flat plate collector from the absorber (3), and enters the tank (3).

Theoretical analysis

In a system linking a solar collector to a heat exchanger, which transfers energy to a storage tank, it is assumed that all the valuable energy collected by the solar collector is fully transferred to the heat exchanger without any thermal loss. The heat transfer rate ($\dot{Q}_{Exchanger}$) within the heat exchanger can be calculated using the following equation:

$$\dot{Q}_{Exchanger} = \dot{m}_{exchanger} C_{p, Exchanger} (T_2 - T_1) \quad (1)$$

where: $\dot{m}_{exchanger}$ – mass flow rate through the heat exchanger, $C_{p, Exchanger}$ – heat capacity of the working fluid in the exchanger.

Without any thermal losses, all heat is exchanged from the collector to the tank, and the thermal energy stored in the tank (\dot{Q}_{tank}) can be calculated using the following equation:

$$\dot{Q}_{tank} = m_{Tank} C_{p, Tank} \frac{\partial T_3}{\partial t} = m_{Tank} C_{p, Tank} \frac{(T_{3\ final} - T_{3\ initial})}{t} \quad (2)$$

where: m_{tank} – mass of the liquid in the tank, $C_{p, Tank}$ – heat capacity of the fluid in the tank, $T_{3\ final} - T_{3\ initial}$: The difference in temperature after the specified duration (t).

m_{Tank} can be determined by:

$$m_{Tank} = \rho V \quad (3)$$

The heat capacity of the working fluid in the tank can be determined using Equations 1 to 3, as shown below:

$$C_{p, Tank} = \frac{\dot{Q}_{Exchanger}}{m_{Tank} \frac{(T_{3\ final} - T_{3\ initial})}{t}} \quad (4)$$

It is to be noted that the Solar Collector Efficiency was estimated according to EN 12974-2:2006, which is outlined by Kovács et al. [2011].

RESULTS AND DISCUSSION

Figure 2 discusses the heat capacity of a nano-ionic liquid with the concentration of nanoparticles within it. The concentration of nanoparticles ranges from 0.00% to 1.00%, with significant observations made at 0.60%. The heat capacity increases from 2.47 kJ/kg·K at 0.0% concentration to a peak of 3.31 kJ/kg·K at 0.60% concentration, representing a 34.01% increase. The enhanced specific heat capacity heat-storage capacities offered by the nanoparticles are responsible for the initial rise in heat capacity. The nanoparticles' efficient dispersion at lower concentrations improves the ionic liquid's thermal characteristics. Beyond 0.60%, the heat capacity decreases due to the formation of nanoparticle aggregates, which reduces the effective surface area for heat transfer. While water has a higher heat capacity (4.2 kJ/kg·K), the unconventional operational temperature range of up to 200 °C of nano ionic liquid makes it promising for heat transfer applications at high temperatures, such as thermal energy storage and industrial cooling systems. While its heat capacity was relatively lower, its thermal stability at higher temperatures was a functional benefit over water in certain applications. This aligns with the findings of Cherecheş et al. [2021],

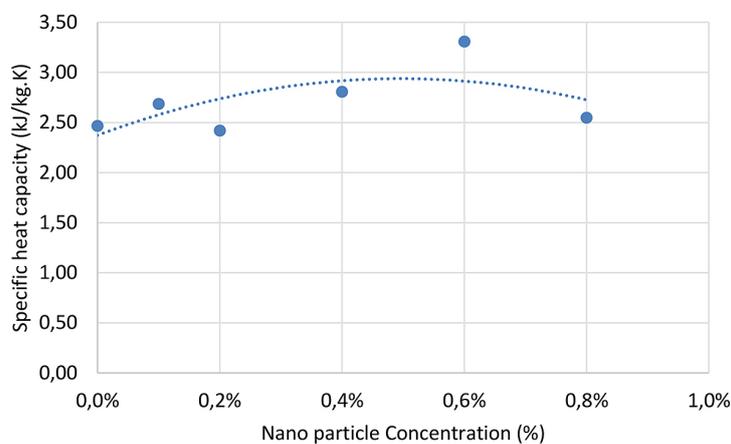


Figure 2. Average heat capacity of the ionic liquids containing different concentrations of nanoparticles

who investigated the specific heat of both ionic liquids and alumina nanoparticle-based nanofluids within a temperature range of 283.15–333.15 K. Their study demonstrated that the specific heat increases with rising nanoparticle concentration, but this trend plateaus beyond a concentration of 2.5 wt.% Al_2O_3 as further nanoparticle loading shows minimal effect. In Figure 3, the average instantaneous efficiency of a solar collector is shown against the concentration of nanoparticles in an ionic liquid. As the nanoparticle concentration increases from 0.00% to 0.60%, there is a notable improvement in efficiency. The efficiency rises to 72.59% at 0.10%, 72.90% at 0.20%, and 72.99% at 0.40% concentration. The highest efficiency, 74.17%, is achieved at a 0.60% concentration. This improvement from 72.16% to 74.17% represents a gain of approximately 2.79%, indicating that adding nanoparticles up to a concentration of 0.60% significantly enhances the solar collector’s performance. Beyond this concentration, no further increase in efficiency is observed.

When comparing this peak efficiency to water’s average instantaneous efficiency of 75.53%,

it becomes clear that the nano ionic liquid falls short by a small margin. The maximum efficiency of the nano ionic liquid at 0.60% concentration is about 1.36% lower than that of water, corresponding to a 1.80% percentage difference. While the nano ionic liquid significantly boosts efficiency, it does not quite reach the water efficiency level. However, the nano ionic liquid’s broader operational temperature range offers advantages in high-temperature applications, potentially compensating for the slight reduction in efficiency compared to water. Therefore, despite water being marginally more efficient, the thermal benefits of the nanoparticle-ionic liquid mixture hold significant practical value. This result agrees with the conclusions of Fathabadi [2020] and Hamdan and Sarsour [2018], who observed that the efficiency of flat plate collectors improves as nanoparticle concentration increases up to an optimum value of nanoparticle concentration, beyond which the efficiency decreases due to the particle agglomeration

The graph in Figure 4 illustrates the impact of varying nanoparticle concentrations on the

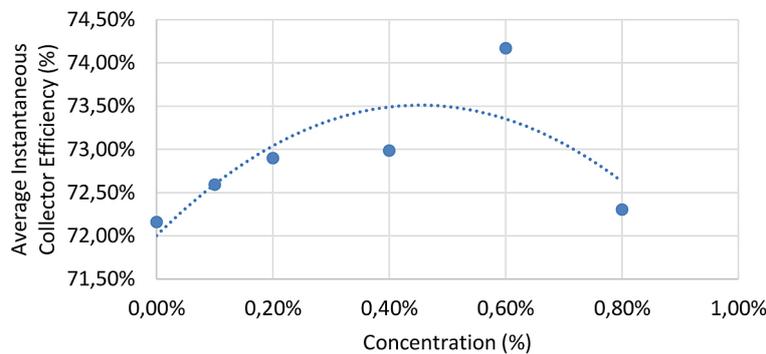


Figure 3. Average instantaneous efficiency of the collector at different concentrations of nanoparticles in an ionic liquid

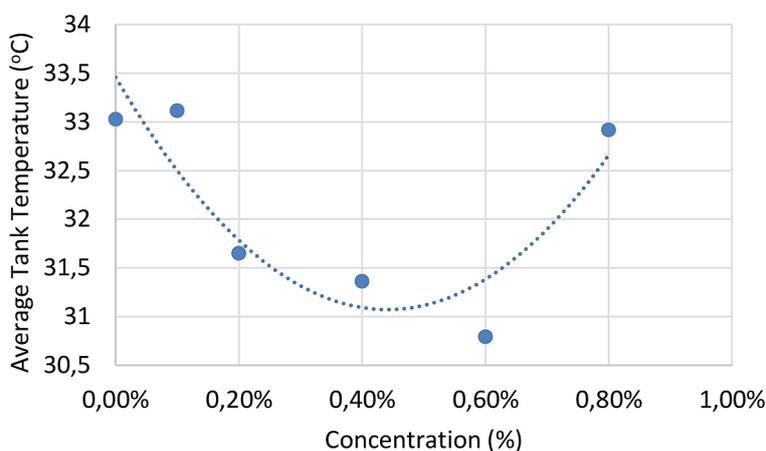


Figure 4. Average hourly tank temperature for different nano-ionic liquids concentrations

average temperature of a thermal energy storage tank. The average tank temperature is seen to decrease significantly as the concentration of nanoparticles increases from 0% to about 0.50%, signifying the enhancement of the heat capacity of the liquid and the efficiency of transferring thermal energy. Notably, with a concentration of 0.50%, the temperature decreases from 33 °C to a minimum of 31 °C (declination of 6.06%). This decrease demonstrates the increased heat capacity with an optimized nanoparticle concentration. However, the average tank temperature increases when nanoparticle concentration exceeds 0.50%, indicating a reduction of heat capacity. An explanation for this decrease could be nanoparticle aggregation or an increase in viscosity, thus decreasing the effectiveness of heat dissipation. This graph exhibits a U-shaped pattern and reveals the necessity of nanoparticle concentration in the range of 0.50% for better thermal performance in energy storage devices.

Water has a higher heat capacity, reaching an average temperature of 37.03 °C. In contrast, the nano ionic liquid at the ultimate concentration reaches a lower average temperature of 31.0 °C (6.03 °C difference). This suggests that precise nanoparticle incorporation is crucial to increasing thermal energy storage efficiency by as much as possible, indicating that significant improvement is achievable with adequate nanoparticle concentration. The initial stage of this figure agrees well with equation (4), and the specific heat capacity decreases with temperature. However, as the concentration of nanoparticles exceeds the optimum value, the nano ionic fluid temperature increases with nanoparticle concentration due to their agglomeration and behavior as large solid particles that absorb heat.

In Figure 5, temperature behaviour in a solar thermal system is presented by comparing the performance of the system components: solar collector, thermal storage tank, and heat exchanger. During the first four hours of operation, temperatures in the collector inlet (T_1), collector outlet (T_2), and storage tank (T_3) all show a steadily increasing pattern, which demonstrates the system's capability of consuming and transferring solar energy. The use of the nano-ionic liquid in the storage tank improves the capacity of heat retention where the T_3 is gradually decreased after shutting off the heat source because this shows the possibility of applying these sophisticated materials to enhance the thermal storage system efficiency, especially when there is a more extended period of heat to be retained.

Additionally, the observed data was subjected to very stable ambient temperature (T_4), indicating that the recorded temperature fluctuations within the overall system were not external environmental anomalies but rather a result of the internal dynamics of the solar thermal setup. This rapid decline in T_1 and T_2 following the shutdown of the pump and lighting unit demonstrates the importance of active circulation in maintaining high temperatures in the system. The experiment proves the practicality of solar thermal systems in environments where reliable and efficient energy capture and storage are necessary. The results could help inform future generations of solar energy technology, highlighting the importance of tailoring the material and operational parameters to deliver the maximum efficiency.

Figure 6 provides a comparative analysis of the thermal performance of a solar thermal system using two different storage mediums: nano-ionic

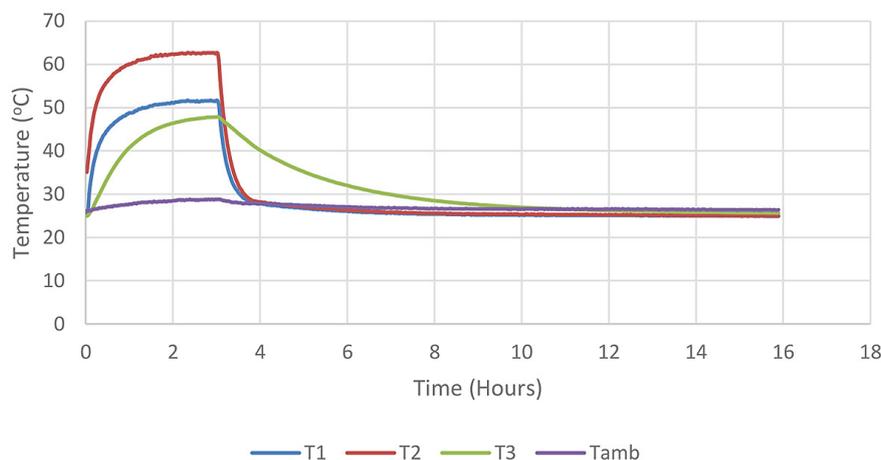


Figure 5. Hourly temperature variation along the ideal concentration nano ionic liquid experiment

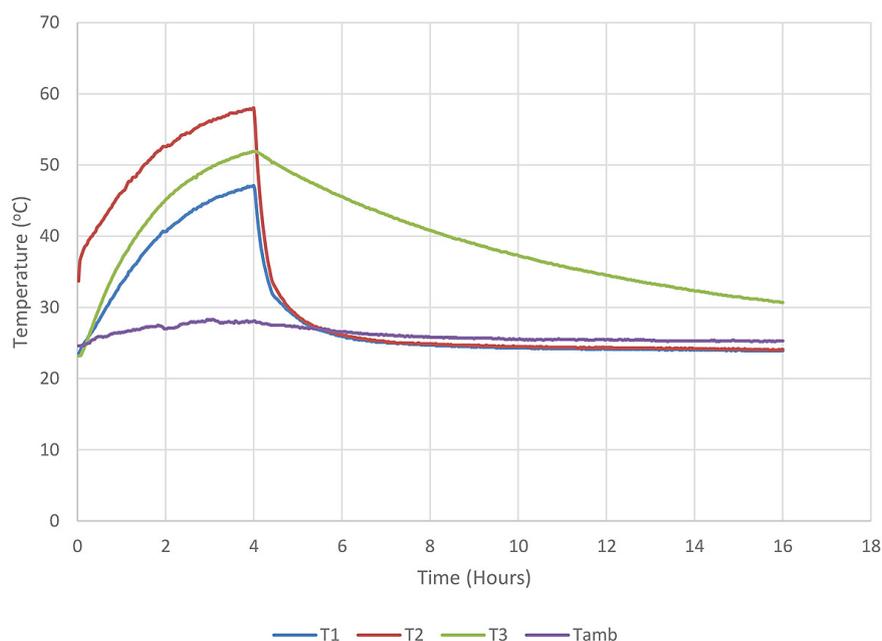


Figure 6. Hourly temperature variation along the experiment of water

liquid and water. For both systems, temperature readings of collector inlet (T_1), collector outlet (T_2), tank (T_3), and ambient (T_4) are taken to evaluate the performance under similar conditions. At the beginning, the starting temperature of the systems is similar, suggesting that experiments were done under the same conditions. As the experiment proceeds, higher temperatures at T_1 and T_2 are observed for the nano-ionic liquid system. This difference is because the lower heat capacity of nano ionic liquid absorbs less heat from the solar collector. Hence, the circulating liquid temperature is elevated.

The higher temperatures in the nano-ionic liquid system at T_3 are due to the higher temperatures at the collector points where it is heated before being pumped into the tank, and it is better than the water-based system. After 4 hours, the tank temperature is slightly higher as the water system absorbs better and retains heat. Consistent with the enthalpy requirement, the water system retains more heat in the storage tank at 16 h than the nano-ionic liquid system. The results indicate that although the lower thermal capacity of the nano-ionic liquid results in higher temperatures in the collector, the increased heat capacity of water leads to better heat absorption and storage in the tank. The comparison demonstrates the importance of choosing proper thermal storage fluids depending on the desired performance characteristics in solar thermal systems.

CONCLUSIONS

The following conclusions reflect the study's key outcome in the present work. The incorporation of copper oxide nanoparticles (CuO) into the ionic liquid 1-Butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF6]) dramatically enhances the thermal performance of solar thermal energy storage systems. The optimal concentration of 0.60% CuO nanoparticles boosted heat capacity by 34%, resulting in an instantaneous efficiency of 74.17%, substantially improving conventional water-based systems.

Nano-ionic liquids have a more comprehensive operational temperature range than water. They can retain the liquid phase up to 200 °C, making them more suitable for high-temperature applications. This quality is conducive to more effective energy storage and retrieval in CSP systems that hold down high temperatures.

Higher concentrations of nanoparticles beyond 0.60% show aggregation and deteriorate thermal performance. This observation further stresses the importance of nanoparticle optimization to ensure high thermal efficiency and avoid diminishing returns.

While nano-ionic liquids are shown to have enhanced thermal properties, water outperforms them based on heat capacity: water attains an average instantaneous efficiency of 75.53%. Nevertheless, nano-ionic liquids' extended operational temperature range and stability compared

to nanostructured inorganic electrolytes provide a practical advantage for specific high-temperature applications, which may compensate for the slight efficiency loss.

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