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Experimental Investigation on Thermal Conductivity and Viscosity of Phase Change Material (NaNO3 and KNO3) with Different Concentrations of ZnO Polymer Nanofluids for Solar Energy Absorption

Sudheesh Chandran R.[1], V.K. Jeba Singh[2]

Abstract

When evaluating the effectiveness of solar heat absorption methods or solar thermal energy storage systems (TESS), heat transfer fluid is a crucial element. Thermal conductivity and usable heat obtained for any industrial or immediate power plant efficiency are improved by the distinctive refining of Heat Transfer Fluid (HFT). The phase change material used in this study, known as solar salt is a blend of 60% $NaNO_3$ *and 40%* KNO_3*. It is prepared as the base solution of HTF and is improved by the addition of* ZnO_3 *polymer nanofluids at different concentrations between 0.01 and 0.05. Utilizing a single HTF as a medium in solar energy absorption systems such as collectors and storing that energy in a TESS for further use in thermal energy generation is the main driving force behind this research. As a result, the amount of heat lost during absorption and storage can be reduced and used for longer. The prepared HTF has undergone experimental examination, and its fluid and thermal characteristics are examined at changes in temperature between 25 and 50 degrees Celsius. After sonicating the various produced solutions for 30 minutes, the experiment was conducted. As a result, a total of 6 samples with volume concentrations of* ZnO_3 *polymer nanofluids as 0.01,0.02,0.03,0.04 and 0.05 were prepared in the research lab, along with a sample without polymer nanofluids. The KD2 Pro setup is used to conduct experiments to evaluate the thermal conductivity and viscosity of the prepared solution at various temperatures, including 25°C, 30°C, 35°C, 40°C, 45°C and 50°C. The outcome of the temperature gradient's effect on thermal conductivity and viscosity demonstrates the Brownian motion of the polymer nanofluids and the enhancement of the solution's thermophoresis. As a result, the research indicates that the HTF's refining for both absorbing solar energy and storing heat energy in TESS has advanced.*

Keywords: Phase change Material, Solar Salt, ZnO, Polymer nanofluids, HTF, Thermal conductivity & Viscosity.

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INTRODUCTION

Power consumption is predicted to rise by 50% between 2021 and 2040 due to the expected two billion additional people on the planet over the next 20 years as well as rising living standards as reported in 2022 International Energy Agency World Energy Outlook. Currently, 66% of the world's energy needs are met by fossil fuels like coal, gas, and oil etc. Once spent, fossil fuels cannot be replenished because they formed in the Earth's crust over millions of years. These fuels will soon run out if we continue to use them and the future generation will be in critical condition. End-of-life fuels are referred to as “non-renewable.” The first resources to run out are oil and gas, followed by coal. The burning of fossil fuels causes the atmosphere to fill with carbon dioxide. Extensive research indicates that our excessive consumption and combustion of fossil fuels is a primary cause of the greenhouse effect and global warming which ultimately leads to climatic changes. Burning coal and gas also releases Sulphur dioxide gas. Sulphur dioxide is a main component of acid rain and can cause respiratory issues for living things. The above all brings the relevance of using renewable energy for power needs. Though our world's present energy demand is high but significantly less than the potential of the planet's renewable energy resources. Renewables will make up a sizable portion of the energy mix in the future in order to improve energy security. Renewable energy, sometimes known as clean energy or green electricity, comes from naturally regenerated renewable resources and doesn't harm the environment such as air, water or climate change etc.

Energy that is sustainable, something that can never run out or be endless, like the sun is how renewable energy sources are defined. The various renewable energy sources are solar energy, wind energy, hydro energy, tidal energy, geothermal energy, biomass energy etc. Of this solar energy is the most widely used renewable energy source based on the geo-location. Primary renewable energy sources like wind and solar shows different energy outputs level during day or night or for particular period or for a season. These variations can be mitigated with long-duration energy storage, which stores excess energy for times when it's needed. This is where molten salt comes into play in energy storage systems via solar energy. The major advantages of molten salts are low costs, non-toxicity, non-flammability, high thermal stabilities and low vapor pressures. It also holds low viscosity, high volumetric heat capacities, and high boiling temperatures which are the characteristics of molten salts. As per literature study molten salts like Sodium Nitrate, Potassium Nitrate, Calcium chloride are suitable both as heat storage medium and optimized ratio can be used as heat transfer fluid (HTF). The power plant efficiency can be improved with optimized HTF as TESS, which runs on Air-Brayton, Brayton, and Rankine cycles are a few of the cycles that can be used to convert thermal energy into electrical power. Many studies by researchers in the recent decades shows the need for better HTF and efficient TESS.

Studies on Molten Salt and TESS

Work done by various researchers in the improvement of Energy absorption and storage has helped to narrow the area of this experimental work. Few researchers work has been discussed for understanding the needs and scope of this research work. [1] conducted studies in TESS with temperature of about 200.0 ºC by creating a composite PCM, with molten salt embedded in nickel foam and they found an increases in PCM's effective thermal conductivity also improvement in latent heat of thermal energy system. [2] also studied about the thermal energy storage material by added SiO_2 in molten salt and their experimental findings reveals that the suggested strategy gives heat storage units with a wider operational temperature range. [3] has also experimented oil as the heat transfer fluid and eutectic salt of 50 weight percent $NaNO_3$ and 50 weight percent KNO_3 with a melting point of roughly 220ºC was used as the PCM for a middle-temperature solar energy application with parabolic-trough solar collector, they concluded that pure eutectic salt, particularly at higher heating temperatures, natural convection was very dominant during heat storage also the presence of metal foam improves process of heat retrieval.

[4] has studied about properties of multi component molten salt consisting of potassium nitrate, sodium nitrite, and sodium nitrate with 5% additive A of the chlorides, they found greater thermal stability with optimal working temperature would rise from 500ºC to 550ºC. [5] done a study on molten salt with SiO_2 nanofluids for TESS, they concluded with result as 15% increase in heat capacity and a 41–429% change in viscosity. Furthermore, there has been notable non-Newtonian behavior in the nanofluids. So, this provides evidence that increased heat capacity and shear-thinning behavior of molten salt nanofluids are mainly caused by dendritic salt of nanostructures.

Lu-lu Zou et al. (2019) studied experimentally on quaternary nitrate as Hitec salt with $Ca(NO_3)_2$ addition and concluded that the Hitec salt with $Ca(NO_3)_2$ addition had greatly changed melting, crystallization, and decomposition points of 83.1°C, 163.1°C, and 628.5°C, respectively. In addition they also achieved a temperature range of 200–565°C with thermal conductivity of 0.655 W/(m K) [6]. Chun lei Wu et al. (2023) has experimentally studied on ternary molten salt combinations for TESS such as NaCl–KCl–LiCl, NaCl–KCl–NaF, and NaCl–KCl–Na_2CO_3, their results reveals that thermal energy storage density exhibited by the eutectic salt NaCl–KCl–Na_2CO_3 is 1.87 and 1.31 times higher than that of other combinations with strong thermal stability even at temperatures as high as 700°C [7]. [8] has experimented and found use of composite phase change material (PCM) improvement up to 42.9% with very good corrosion resistance compared to non-composite PCM. [9] also focused on composite PCM with expanded graphite (EG) and three binary molten salts combinations like $LiNO_3$–KCl, $LiNO_3$–$NaNO_3$, and $LiNO_3$–NaCl, they narrowed the optimization with thermal conductivity increased by 4.9–6.9 times and also composite PCM exhibited greater homogeneity [9].

Chun lei Wu et al. (2023) has also studied on composite phase change materials of NaCl-KCl-NaF with nanofluids as CuO and Al_2O_3 nanofluids in varying ratios. They experimental found adding 0.5 weight percent Al_2O_3 and 0.5 weight percent CuO nanofluids to the base salt produced better results with increase in thermal conductivity by 3.70 compared to base salt without nanofluids [10]. Haoran Wang et al. (2022) studied on high-temperature PCM with composite as ternary salt which was made up of 50% sodium chloride (NaCl), 30% potassium chloride (KCl), and 20% magnesium chloride ($MgCl_2$), they noted the thermal conductivity increased six times higher with better shape stability [11, 12]studied on binary nitrate salt with silica nanofluids experimentally and found 20 nm nanofluids showed the greatest increase in average specific heat capacity by about 26.7%.

[13] examined how the size of SiO_2 nanofluids affect thermo-physical characteristics and stability of molten binary nitrate salt, their investigation shows that nanofluids with nanofluids bigger than 450 nm are more stable than ones with nanofluids smaller than 27 nm also found increase in viscosity for particles larger than 450 nm was insignificant, in contrast to the case of 27 nm particles [13, 14] has studied and concluded that nanofluids are the most effective option for increasing the specific heat capacity (up to 60%) and thermal conductivity (to 120 percent) of TESS with 1 weight percent concentration of nanofluids. So this shows the impact of nanofluids in TESS for storing heat energy. Xueming Yang et al. (2022) experimentally done a performance study on ternary carbonate Li_2CO_3: Na_2CO_3: K_2CO_3 with 31:34:35 mass ratio with ZnO nanofluids. The ZnO nanofluids based on ternary carbonate salt that were synthesized showed improved heat capacity, decreased corrosivity, and superior thermal stability [15]. Thus, the role of nanofluids in molten salts has a huge impact in thermo physical properties. Hence in this experimental study the molten salt chosen as $NaNO_3$ and KNO_3 with nanofluids as ZnO which can act as a binary role in HTF and TESS.

EXPERIMENTAL WORK

As many researchers narrowed the HTF study with the addition of different nano particles, hence this experimental study focused on the Solar salt addition such as 60% $NaNo_3$ and 40% KNo_3 along with the ZnO Polymer nanofluids with different concentration. The Experimental work has divided as Nano solution preparation, next blending with the Molten salt in correct proportion for preparing 6 different samples, then sonication process and finally testing for thermal conductivity, viscosity and Heat absorption rate for different temperatures ranging from 25ºC to 50ºC.

Polymer Nanofluids Preparation

Zinc oxide Nano fluid with concentration range of 0.01 – 0.05 was prepared in the lab from Nano Research Lab in Jharkhand, India. The nano particles are also tested for its Zinc oxide presence using XRD as shown in Figure 1 and Figure 2 shows the TEM analysis during 100 nm scanning level for determine the morphological study of nano particles and chemical compositions of the particle's presence. The size of ZnO nano particles lies between 30-50 nm with 99.9% Purity. Table 1 shows the morphological results obtained from TEM analysis which is spherical in shape with milky white power form of particles. Table 2 shows the purity of Zinc oxide nano particles and the presence of traces of other elements.

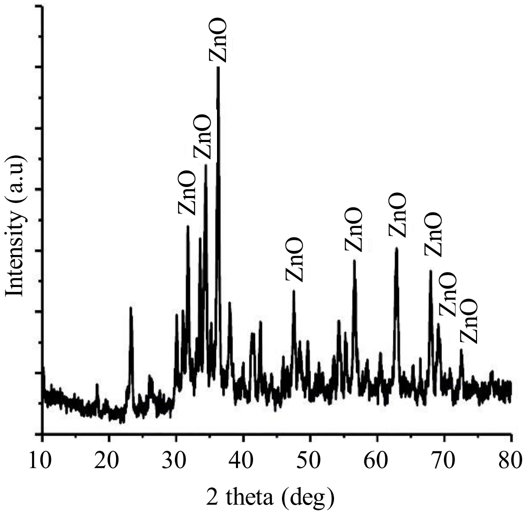

Figure 1. XRD result of ZnO Polymer nanofluids.

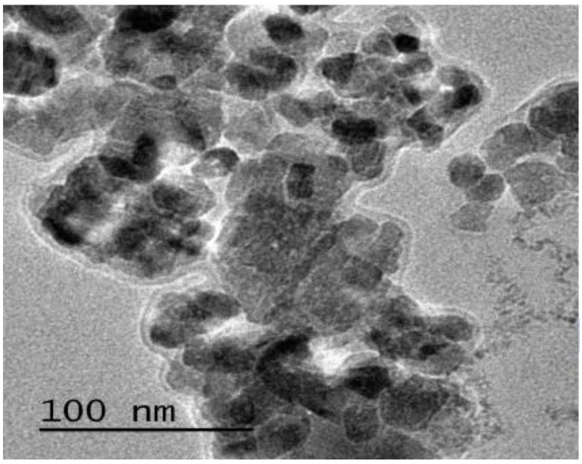

Figure 2. TEM Analysis of ZnO Polymer nanofluids.

Table 1. TEM properties of ZnO polymer nanofluids.

Color	**Milky White**
Form	Powder
Average particles Size	30-50 nm
Morphology	Nearly Spherical

Table 2. Percentage Analysis of ZnO polymer nanofluids.

ZnO	**Pb**	**Si**	**Mn**	**Cu**
> 99.9%	< 0.01%	< 0.02%	< 0.02%	< 0.01%

Combination of ZnO with Molten Salt

Molten salt $NaNO_3$ and KNO_3 are diluted in a litre of distilled water with the ratio of 60:40, for preparing base fluid then measured to correct quantity for mixing with already prepared polymer nanofluids. Since in this experimental work ZnO nano fluid is prepared separately with different volumetric concentration of 0.01, 0.02, 0.03, 0.04 and 0.05 in research laboratory, it is added to the

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measured base fluid samples. Thus, six Samples are prepared which includes a sample without adding polymer nanofluids shown in Figure 3. The 5 different samples named as ZnO-1, ZnO-2, ZnO-3, ZnO-4, and ZnO-5 with different volumetric concentration of ZnO as shown in Figure 4 below. Then the prepared solution is kept in sonication for 30 minutes as shown in Figure 5 and 6.

Table 3 shows the general physical and thermal properties of fluid prepared for HTF and TESS. The tabulated readings show ZnO holds better thermal conductivity, hence it can absorb better heat transfer rate which can be very much useful for solar heat absorption.

Figure 3. Nano fluid Preparation

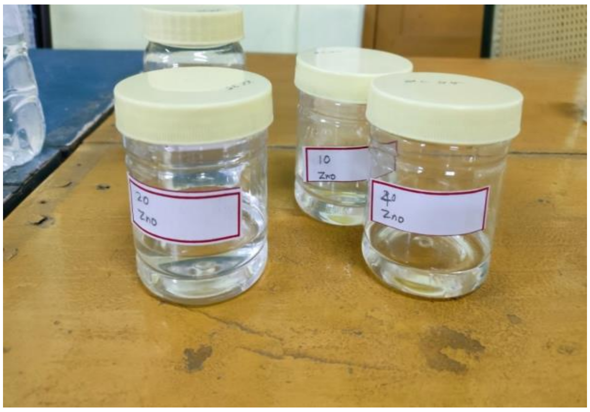

Figure 4. ZnO Samples Prepared.

Figure 5. Power Sonic 410.

Figure 6. Sonication Process.

Table 3. The features of distilled water and polymer nanofluids

Property	**Symbol**	**Unit**	**Distilled water**	**ZnO**
Density	ρ	g/m^3	0.9982	6
Specific Heat	C_p	J/g-°C	4.186	0.494
Thermal Conductivity	K	W/mk	0.599	23.4
Viscosity	μ	cP	1	-
Melting Point	-	°C	0	1,975
Boiling Point	-	°C	100	2,360

Viscosity Measurement

Brookfield-DV-II + PRO viscometer is used to measure viscosity experimentally. Figures 7 shows the schematic diagram with the required components, and Figure 8 shows the experimental setup of device respectively. The Brookfield-DV-II + PRO viscometer works on the basis of driving a spindle through a calibrated spring while it is dipped in the polymer nanofluids sample. By measuring the spring deflection, one may determine the fluid's viscous drag against the spindle. A rotating transducer is used to measure the deflection of springs. The dynamic viscosity readings are noted in Centipoises (Cp). As previously noted, the viscosity of several polymer nanofluids combinations is measured at 25, 30, 35, 40, 45 and 50 degrees Celsius, respectively. The result findings are tabulated, and their impacts are discussed in result analysis session.

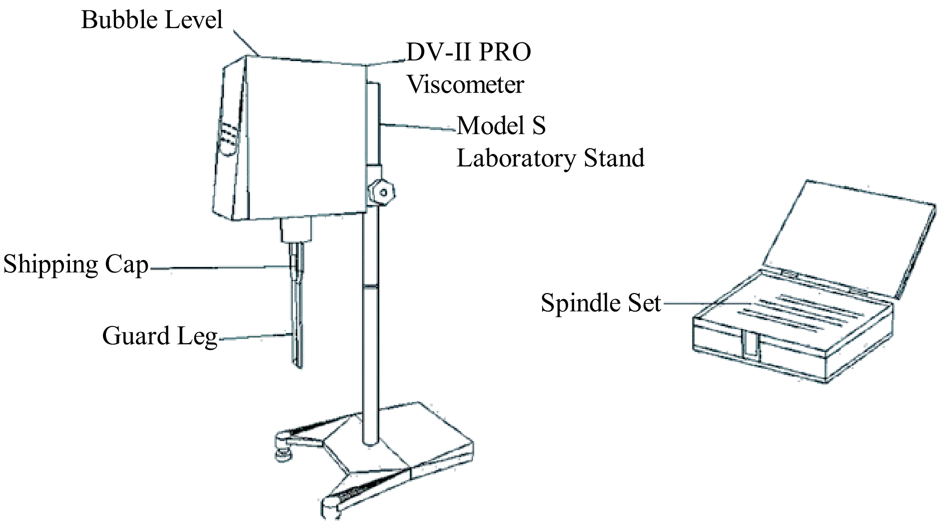

Figure 7. Brookfield–DV-II + PRO Viscometer Schematic diagram.

Figure 8. Brookfield–DV-II + PRO Viscometer in picture.

Thermal Conductivity Measurement

The KD2 Pro thermal properties analyzer, made by Decagon Devices Inc., was used to evaluate thermal conductivity at different temperatures shown in Figure 9. Its sensor can measure temperatures between -50 and +150 degrees Celsius. Thermal conductivity is measured using a tiny single needle

KS-1 sensor, measuring 6 cm in length and 1.3 mm in diameter. All of the aforementioned polymer nanofluids' thermal conductivity has been tested at 20, 25, 30, 35, 40, and 45 degrees Celsius, respectively. As the HTF plays a maximum role in any concentrated collector for absorbing solar heat energy from morning 10 am to evening 4 pm in our geographical area, the temperature chosen was maximum 50ºC. The values are listed in a table.

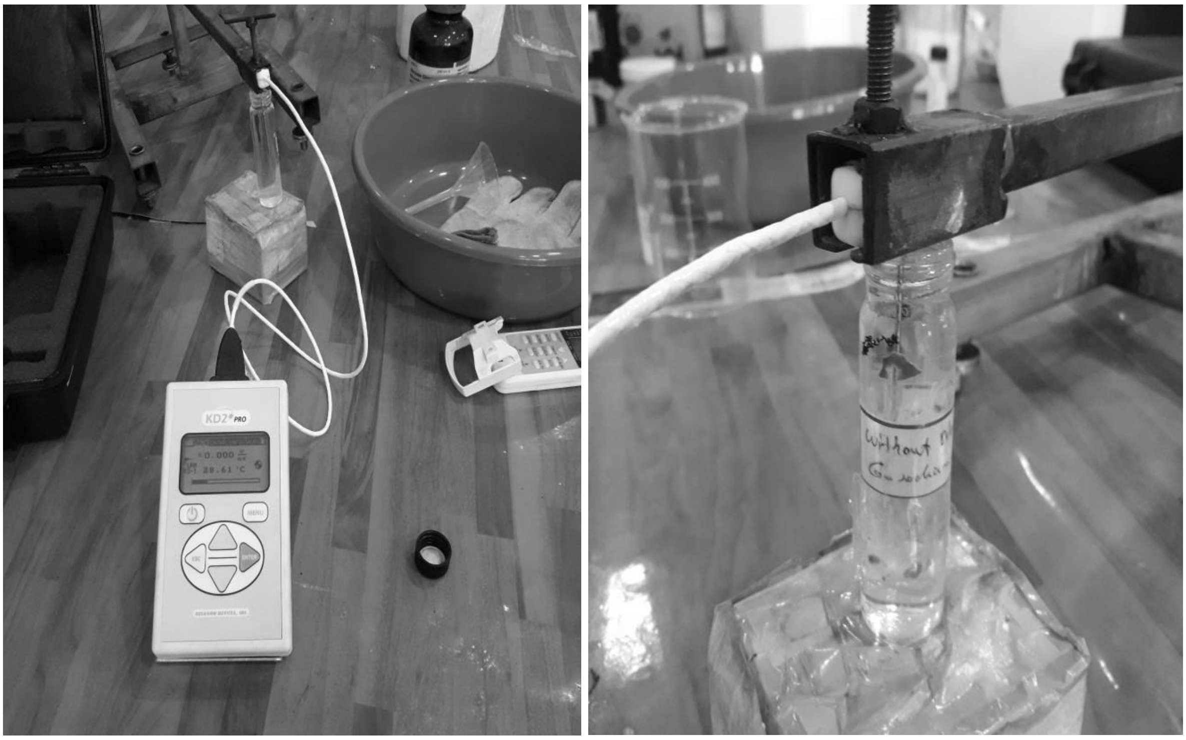

Figure 9. Experimental measurement of thermal Conductivity with KD2 Pro thermal properties analyzer.

Mathematical Calculations

In General, renewable energy extraction is one of the toughest processes similarly storing those energy without much loss is another hardest work. Hence the following theoretical calculations are used to determine the Rate of useful heat gained, total heat losses, Efficiency of Heat absorption for different samples, effect of ZnO polymer nanofluids are shown below, [1] The steady state thermal energy balance equation has the following form:

$$Q_u = Q_{Abs} - Q_{loss} \quad (1)$$

In the equation $Qu = Q_{Abs}-Q_{loss}$, Qu represents the usable energy acquired from Q_{Abs}.

The entire quantity of solar energy captured, Q_{Abs}, is determined by subtracting losses from convection and irradiation between the environment and the collector, whereas Q_{loss} is the total amount of energy lost between the collectors and the surrounding atmosphere.

$$Q_{loss} = U_L A_C (T_M - T_a) \quad (2)$$

where U_L denotes the total heat transfer coefficient, A_C denotes the collector's surface area, and T_M and T_a denote the mean plate temperature and the surrounding air temperature, respectively.

$$Q_u = mC_P (T_o - T_i) \quad (3)$$

The working fluid's output temperature (To), inlet temperature (Ti), and heat capacity (Cp), which can be either water or a polymer nanofluids, are all expressed in degrees Celsius. Calculations for the additional useable energy include

$$Q_u = A_C F_R (I_T (\tau\alpha) – U_L (T_i – T_o) \quad (4)$$

Where I_T is solar radiation and F_R is the heat removal factor, which is the ratio of useful heat gained to energy obtained if the interface temperature of the collector is the same as the inlet temperature. By using the following equation, F_R can be determined.

$$F_R = \frac{mCp(T_o - T_i)}{Ac(I_T(\tau\alpha) - U_L(T_i - T_a)} \quad (5)$$

The sum of the irradiation that the collector has received is computed as:

$$q_{rr} = I_T A_C \quad (6)$$

[2] The ratio between the rates of usable heat (Qu) transferred by solar radiation on the solar heater is referred to as solar thermal efficiency. The following formula can be used to determine thermal efficiency.

$$\eta = \frac{Q_u}{I_T I A_C} \quad (7)$$

The exergy efficiency, which is defined as the maximum output a system can produce given the ambient temperature, may be calculated using the following equation.

$$\eta_{ex} = \frac{1 - T_a\, S_{gen}}{[1 - (T_a/T_s)]q_{abs}} \quad (8)$$

The polymer nanofluids thermal conductivity is created by combining the thermal conductivities of the base fluid and polymer nanofluids [3]. The calculation of the characteristics of polymer nanofluids is done using the following modified equation.

$$K_{nf} = (1 – \varphi)k_{bf} + \varphi\, k_{nf}\beta \quad (9)$$

where K_{nf}, K_{bf}, and K_s are, respectively, the thermal conductivity of the base fluid, the polymer nanofluids, and the polymer nanofluids. The concentration of the polymer nanofluids volume is provided by the formula given below.

$$\varphi = \frac{\frac{W_{nf}}{\rho_{bf}}}{\frac{W_{nf}}{\rho_{nf}} + \frac{W_{bf}}{\rho_{bf}}} \quad (10)$$

Polymer nanofluids's specific heat and density can be represented as:

$$C_{PNF} = \frac{(1-\varphi)\rho_{bf}Cp_{bf} + \varphi\rho_s Cp_s}{\rho_{nf}} \quad (11)$$

$$\rho_{nf} = \rho_{np}(\varphi) + \rho_{bf}(1 – \varphi) \quad (12)$$

The above discussed mathematical calculations are referred from Engy Elshazly et al. (2023) [16], which can be useful for determining the useful heat absorption, heat losses and general instantaneous efficiency of the HTF in solar energy absorption.

RESULTS AND DISCUSSIONS

Experimental readings of thermal conductivity and viscosity are tabulated initially on sample 1 with only base solution and other samples 2,3,4,5 and 6 with Zno Polymer nanofluids with concentration varying from 0.01 – 0.05. Samples with nano ZnO particles shows better heat absorption rate as thermal conductivity increased when compared to the sample without polymer nanofluids. Table 4 shows the readings of thermal conductivity for 6 different samples at different temperature ranges from 25°C to 50°C. Average thermal conductivity of base fluid without polymer nanofluids is 0.5306 and for samples 2,3,4,5,6 is 0.5775, 0.6035,0.6226, 0.6288, 0.6271 which shows a better absorption rate and shows a maximum gain of 15.50% improvement at sample 5 with addition of ZnO at concentration of 0.04 or 4%.

Table 4. Response of Thermal Conductivity for different Temperature.

Temperature (°C)	Thermal Conductivity (W/mK)					
	Sample 1 (Without Nano Particles)	*Sample 2 with 10% ZnO*	*Sample 3 with 20% ZnO*	*Sample 4 with 30% ZnO*	*Sample 5 with 40% ZnO*	*Sample 6 with 50% ZnO*
25	0.518	0.557	0.576	0.609	0.613	0.617
30	0.521	0.561	0.589	0.611	0.616	0.619
35	0.528	0.57	0.599	0.621	0.624	0.621
40	0.532	0.581	0.609	0.623	0.631	0.629
45	0.54	0.591	0.621	0.635	0.641	0.638
50	0.545	0.605	0.627	0.637	0.645	0.641

Table 5. Readings of Viscosity at different temperature.

Temperature (Degree Celisus)	Viscosity (Centipoise)					
	Sample 1 (Without Nano Particles)	*Sample 2 with 10% ZnO*	*Sample 3 with 20% ZnO*	*Sample 4 with 30% ZnO*	*Sample 5 with 40% ZnO*	*Sample 6 with 50% ZnO*
25	1.24	1.33	1.29	1.42	1.41	1.44
30	1.2	0.96	1.12	1.29	1.11	1.04
35	1.03	0.93	0.9	1.02	0.97	1
40	0.87	0.87	0.88	0.94	0.88	0.89
45	0.82	0.8	0.85	0.82	0.81	0.78
50	0.75	0.71	0.78	0.79	0.72	0.74

Table 5 Shows the effect on viscosity due to the change in temperature. Initially the base solution sample tested for varying temperature, then tested for other 5 samples with ZnO polymer nanofluids. The result interpreted from the experimental reading shows the addition of polymer nanofluids has created minor impact compared to the base fluid initially but further the increase in temperature doesn't show much effect due to the presence of ZnO.

The Figure 10 (a) shows the variations observed in viscosity from the experimental result. Though the viscosity decreases as the temperature increases the effect of Zinc oxides presence doesn't reflect big difference compared to the result of base solution sample results. Figure 10 (b) shows the effect of thermal conductivity in 6 samples and the influence of ZnO polymer nanofluids shows big variations with increase in maximum thermal conductivity of 15.50% compared to the base solution without ZnO polymer nanofluids.

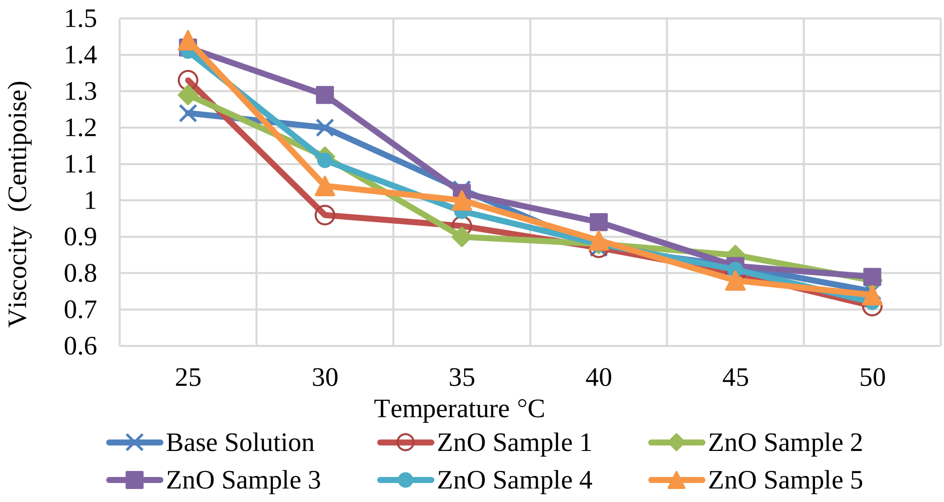

Figure 10. (a) Temp. Vs Viscosity graph with variable percentage of ZnO.

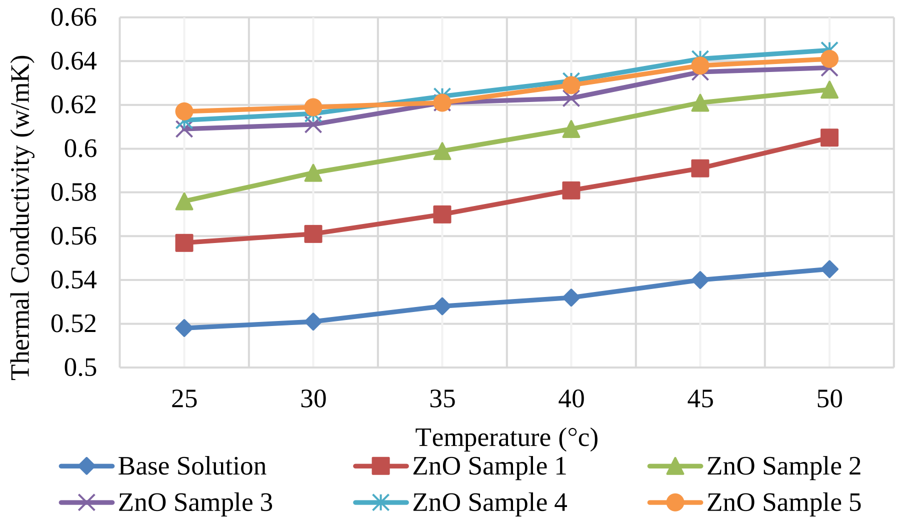

Figure 10. (b) Temp. Vs Thermal Conductivity graph with variable percentage of ZnO.

CONCLUSION

The generated solutions characteristics have changed favorably as a result of phase change material and polymer nanofluids experiments. When compared to materials without polymer nanofluids, the fundamental characteristics of samples containing ZnO particles allow them to conduct and absorb more heat energy. After sonication, It is discovered that the mixing of the polymer nanofluids that were added to the molten salt as polymer nanofluids was more stable. Many researchers have already experimented with mixing polymer nanofluids in any fluid that requires a substrate, such as ethylene glycol, to maintain stability. According to the experimental investigation, viscosity in five examined polymer nanofluids samples did not significantly affect the property of fluid when compared to a sample without polymer nanofluids, indicating that these fluids adhere to Newton's law of fluids. However, when compared to the sample that merely used melted salt as the base fluid, the sample that had ZnO polymer nanofluids addition at a concentration of about 0.04 showed a greater improvement of roughly 15.50% in terms of thermal conductivity. In addition, the total heat absorption efficiency has risen by 7.6 when compared to the HTF without the inclusion of ZnO polymer nanofluids. Therefore, this suggested sample can be utilized directly as a working fluid in any TESS and can also function as a HTF in any solar concentrated collector.

Nomenclature

ZnO: Zinc Oxide

PCM: Phase Change Material ZnO–1: Solar Salt Solution + 1 wt% Zinc Oxide

CSP: Concentrated Solar Power ZnO–2: Solar Salt Solution + 2 wt% Zinc Oxide

$NaNO_3$: Sodium Nitrate ZnO–3: Solar Salt Solution + 3 wt% Zinc Oxide

KNO_3: Potassium Nitrate ZnO–4: Solar Salt Solution + 4 wt% Zinc Oxide

TESS: Thermal Energy Storage System, ZnO – 5 : Solar Salt Solution + 5 wt% Zinc Oxide

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