

THERMAL PROPERTIES ON NANOFLUIDS BASED ON A HIGH TEMPERATURE-HEAT TRANSFER FLUID AND METALLIC NANOPARTICLES FOR CONCENTRATING SOLAR ENERGY

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ABSTRACT

In this work, nanofluids were prepared using commercial Cu nanoparticles and a commercial Heat Transfer Fluid (eutectic mixture of diphenyl oxide and biphenyl) as the base fluid. This fluid is used in Concentrating Solar Power plants. Different properties such as density, viscosity, heat capacity, and thermal conductivity were characterized. Nanofluids showed enhanced heat transfer efficiency. In detail, the incorporation of Cu nanoparticles led to an increase of the heat capacity up to 14%. Also, thermal conductivity was increased up to 13%. Finally, the performance of the nanofluids prepared increased up to 11% according to the Dittus-Boelter correlation.

INTRODUCTION

Concentrating Solar Power is one of the most interesting alternative to conventional energy sources. But actually, it is necessary to improve the global efficiency of these plants in order to decrease the costs of the energy production. Thus, there are many lines of research to improve the efficiency of this technology. In plants based on parabolic mirrors, a thermal fluid flowing through a tube covered with a coating capable of absorbing radiation is used. The absorbed radiation heats the thermal fluid. One option to improve the efficiency of these plants is to improve properties of the Heat Transfer Fluid (HTF) usually used. It is well-known that the suspension of solids in liquids can improve some thermal properties of the liquid [1-3]. Specifically, colloidal suspension of some kind of nanostructures, such as nanoparticles, nanotubes, nanofibers, nanorod, in a base fluid is known as nanofluids [4]. An increase of the thermal conductivity of nanofluids based on metallic nanoparticles have been reported [1,2,5-7]. Also, for applications at lower temperature, nanofluids based on water and ethylene glycol as base fluid, and metallic nanoparticles have been studied [2,8]. In turn, the use of metal oxide nanoparticles has been reported too [2,9]. But, there are many studies related with lower temperature applications using water and ethylene glycol, but analysis of the nanofluids based on the HTF used in Concentrating Solar Power plants is clearly needed.

So, in this work, we report the preparation of nanofluids based on Cu nanoparticles and a HTF used typically in CSP plants as the base fluid. The nanofluids were prepared using the two-step method, and several properties were characterized such as density, viscosity, heat capacity, and thermal conductivity. The analysis of the heat transfer for the nanofluids prepared in relation to the base fluid was developed. We observed that the Cu nanofluids improved the thermal properties and the heat transfer coefficient compared with the HTF.

EXPERIMENTAL

In this work, nanofluids based on Cu nanoparticles and a commercial Heat Transfer Fluid were prepared using a two steps method [10]. This method consists in the use of the previously synthesized nanoparticles and a base fluid used as a HTF. The base fluid used was the eutectic mixture of diphenyl oxide (73.5%) and biphenyl (26.5%). This was supplied by The Dow Chemical Company©, model Dowtherm A. Figure 1 shows the main properties of this fluid, that is the evolution of vapour pressure, density, viscosity, heat capacity and thermal conductivity with respect of the temperature. This fluid is used in some CSP plants in the southern of Spain. The properties shown in Figure 1 give us information of the reason for its use in this kind of plants. For example, the low vapour pressure or the high heat capacity are interesting properties for this application. On the other hand, the Cu nanoparticle (purity 99.5%, density 8940 kg/m³ at room temperature) used were supplied by Sigma-Aldrich©, and they show a particle size of 40-60 nm.

Nanofluids were prepared according to the next procedure. A nanofluid with a Cu concentration of 0.01wt.% was prepared. From this, nanofluids with a concentration of 0.5·10⁻⁴, 1.0·10⁻⁴ and 5.0·10⁻⁴ wt.% were prepared. The nanofluids were prepared under sonication for 3 h using a Sonics Vibra Cell VCX 750 sonicator.

On the other hand, several properties of the nanofluid prepared such as density, viscosity, heat capacity and thermal conductivity were characterized in order to evaluate the heat transfer performance. Density was determined using a pycnometer thermostated using a thermal bath supplied by

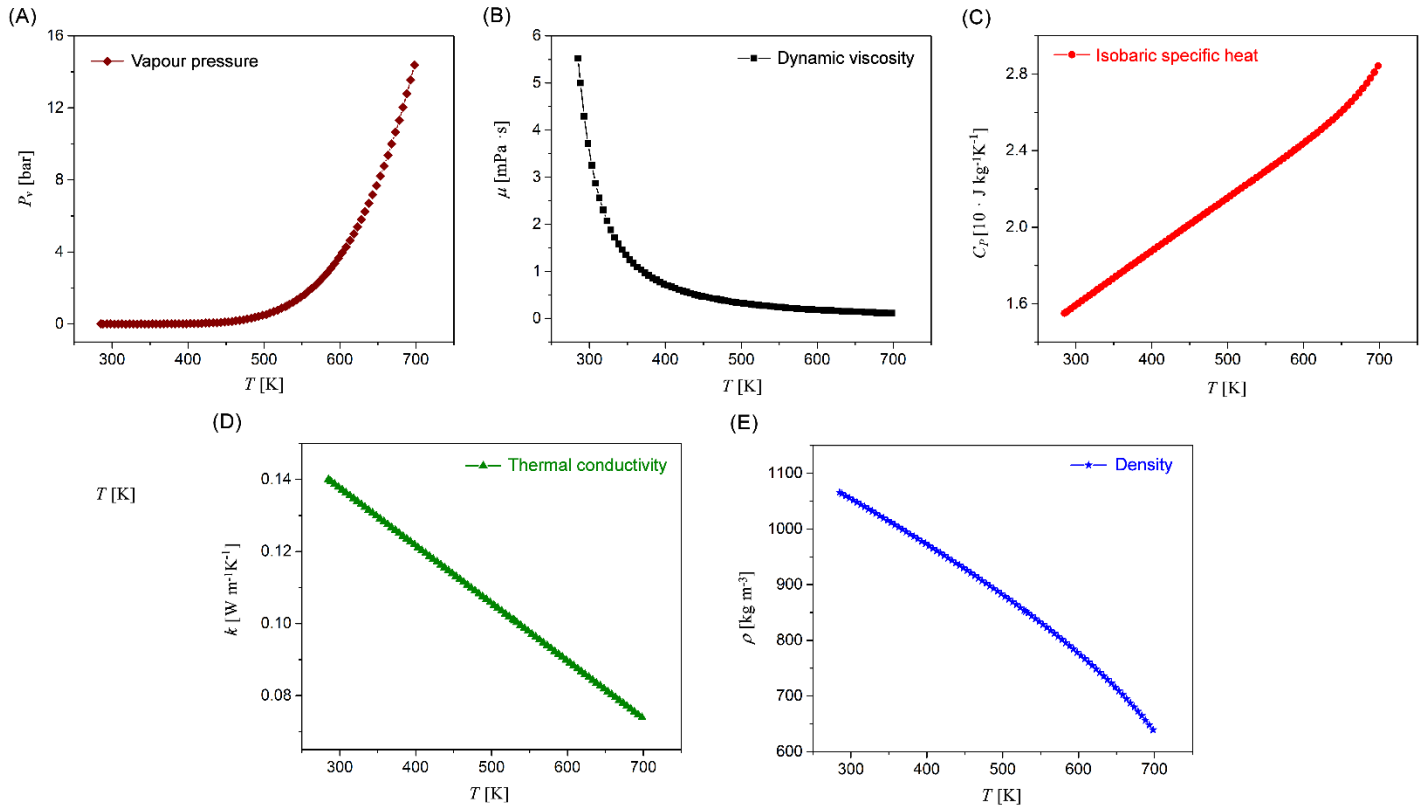


Figure 1 Evolution of the vapour pressure (A), dynamic viscosity (B), heat capacity (C), thermal conductivity (D) and density (E) with respect of the temperature of the heat transfer fluid used as the base fluid in the nanofluids prepared.

Select©. Dynamic viscosity was estimated using a SV-10 viscometer supplied by Malvern©. Also, heat capacity was determined using the Temperature Modulated Differential Scanning Calorimetry (TMDSC) technique. The system used was supplied by TA Instruments©, model Q-20. Finally, thermal conductivity was determined using the flash technique. The equipment was supplied by Linseis Thermal Analysis©, model LFA 1600. All properties were determined for the base fluid for comparison purposes. From the values obtained for these properties, an analysis of the heat transfer performance was developed according to the Dittus-Boelter correlation (see equation (1) below).

RESULTS AND DISCUSSION

One option to evaluate the efficiency of the nanofluids is to determine the ratio of the heat transfer coefficient between the nanofluids prepared and the base fluid used. This can be evaluated using the Dittus-Boelter correlation [11], which gives the ratio of the heat transfer coefficient (h_{nf}/h_{bf}) as

$$\left(\frac{h_{nf}}{h_{bf}}\right) = \left(\frac{\rho_{nf}}{\rho_{bf}}\right)^{0.8} \left(\frac{k_{nf}}{k_{bf}}\right)^{0.6} \left(\frac{C_{P(nf)}}{C_{P(bf)}}\right)^{0.4} \left(\frac{\mu_{nf}}{\mu_{bf}}\right)^{-0.4} \quad (1)$$

where h is the heat transfer coefficient, ρ is the density, C_P is the heat capacity, and μ is the dynamic viscosity [11,12]. In turn,

nf is related to nanofluids, and bf is related to the base fluid. Thus, when $h_{nf}/h_{bf} = 1$, the system shows the same behaviour of the base fluid. But when $h_{nf}/h_{bf} > 1$, the performance of the system analysed is enhanced with respect to the performance of the base fluid used. Therefore, in order to evaluate the ratio of the heat transfer coefficients, density, thermal conductivity, heat capacity, and dynamic viscosity were measured.

In order to improve the understanding of the results exposed, the nanofluids prepared are named as Cu0.5, Cu1.0 and Cu5.0, being the number the Cu nanoparticle mass fraction $/10^{-4}$ (see Experimental section)

Density

Figure 2 shows the values of density obtained for the nanofluids prepared and for the base fluid measured at room temperature. The value reported for the base fluid was measured following the same procedure. This value is comparable with the value reported for the base fluid by the supplier.

It is possible to observe an increase of the density values up to 0.21% for the highest mass fraction, which can be positive for the performance for the heat transfer process, as reported previously [13,14]. In turn, the increase of the density values is slightly, probably because the nanoparticle mass fraction was low. Also, the increase of the density values did not follow a linear trend with respect of the nanoparticles mass fraction, which is a typical behaviour when the nanoparticles interact between them and the internal morphology of the system is

changing. So, the increase of the concentration can produce agglomerations of the nanoparticles and therefore can change the trend of the density.

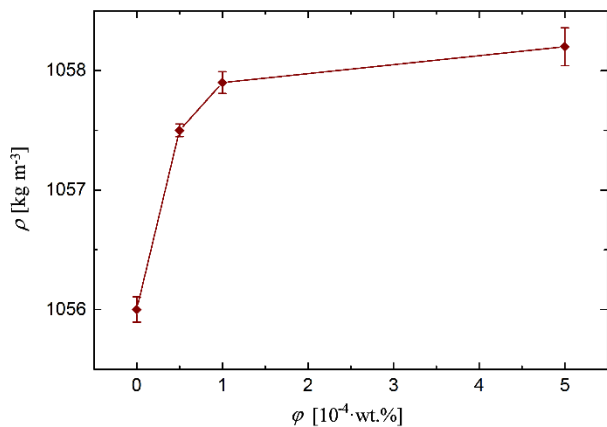


Figure 2 Density values for the nanofluids prepared with respect to Cu nanoparticles mass fraction, ϕ .

Thermal conductivity

Thermal conductivity was measured at several temperatures between room temperature until 373 K, approximately. Figure 3 shows the values of the thermal conductivity for the nanofluids prepared. Also, the values of thermal conductivity of the base fluid are included in Figure 3 for comparison purposes. These values are provided by the supplier. In order to check the methodology used, thermal conductivity for the base fluid was measured too. The deviation between the values reported by the supplier and the values measured in our lab for the base fluid is less than 1.5%.

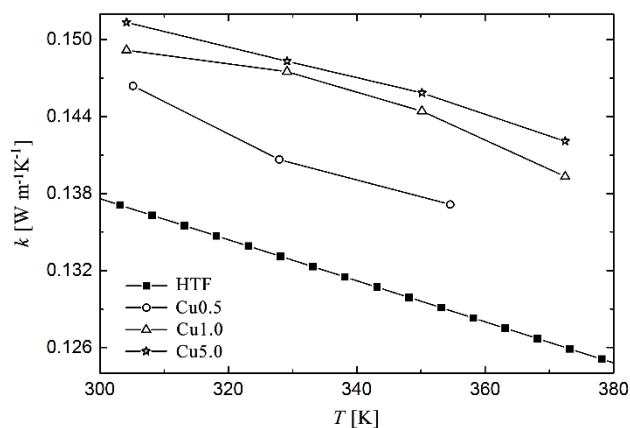


Figure 3 Thermal conductivity values for the nanofluids prepared with respect to temperature. The values for the base fluid reported by the supplier are included for comparison purposes.

The values obtained showed an increase in thermal conductivity up to 13%, approximately. Materials with high thermal conductivity show higher heat transfer efficiency

[13,15] and the suspension of nanoparticles in a base fluid shows an increase if the thermal conductivity in some cases [1,2]. Thus, in our case, the incorporation of Cu nanoparticles to the base fluid used increased thermal conductivity which can lead to increase in the heat transfer performance. In order to evaluate this increase, the ratio between thermal conductivity for the nanofluid and for the base fluid (k_{nf} / k_{bf}) was determined. Therefore, Table 1 shows the values of the ratio of the thermal conductivity values obtained.

Table 1 Values of the ratio of the thermal conductivity (k_{nf} / k_{bf}) for the nanofluids prepared.

ϕ [wt.%]					
$0.5 \cdot 10^{-4}$		$1.0 \cdot 10^{-4}$		$5.0 \cdot 10^{-4}$	
T [K]	k_{nf} / k_{bf}	T [K]	k_{nf} / k_{bf}	T [K]	k_{nf} / k_{bf}
305.2	1.07	304.2	1.09	304.2	1.11
328.0	1.06	329.2	1.11	329.2	1.12
354.6	1.06	350.2	1.11	350.2	1.13
		372.5	1.11	372.5	1.13

Also, all the nanofluids prepared followed the same trend that the base fluid, that is the higher temperature the lower thermal conductivity.

Heat capacity

The heat capacity was measured for the nanofluids prepared at several temperatures between room temperature until 373 K, approximately. Figure 4 shows the values obtained. The plot of the heat capacity values for the base fluid provided by the supplier are included for comparison purposes. In turn, the heat capacity for the base fluid was measured following the same procedure in order to check the methodology used. The deviation with respect of the values provided by the supplier was about 1%.

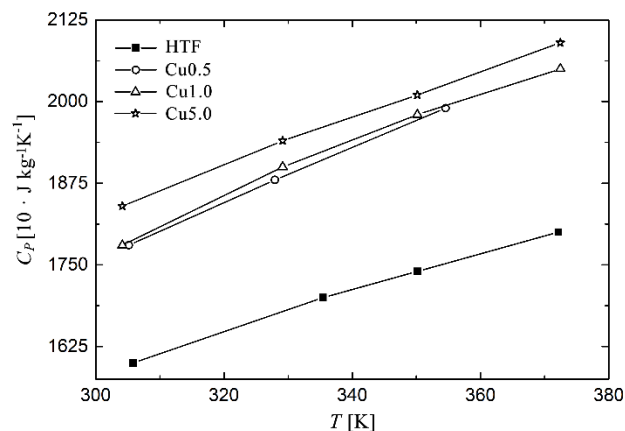


Figure 4 Heat capacity values for the nanofluids prepared with respect to temperature. The values for the base fluid reported by the supplier are included for comparison purposes.

So, heat capacity increases for the nanofluids prepared with respect of the base fluid up to 14%, approximately. The increase of the heat capacity when nanoparticles are incorporated into a

HTF has been reported previously [16,17], but the opposite behaviour have been found too [9,13] and this has been explained for the low heat capacity of the solids with respect to the liquids. But, the behaviour found in our nanofluids can be due to a certain internal structure of the base fluid molecules around the nanoparticle, which leads to a positive order of the system [18,19].

From the values of heat capacity, it is possible to obtain the volumetric heat capacity (C_{PV}) according to

$$C_{PV} = \rho C_P \quad (2)$$

Volumetric heat capacity is interesting because the heat transfer velocity (\dot{q}) in a heat exchanger depends on C_{PV} according to

$$\dot{q} = \dot{V} C_{PV} \Delta T \quad (3)$$

where \dot{V} is the flow volume, and ΔT is the difference in temperature [9]. So, measuring the density at the approximated temperature of the heat capacity measurements, the value of the volumetric heat capacity were determined. These values are shown in Figure 5. The evolution is similar to that of the heat capacity, due to the low concentration of nanoparticles in the nanofluids prepared, which leads to small variations in density. Thus, for the same difference in temperature and similar flow volume, the nanofluids prepared showed higher heat transfer velocity than the fluid base.

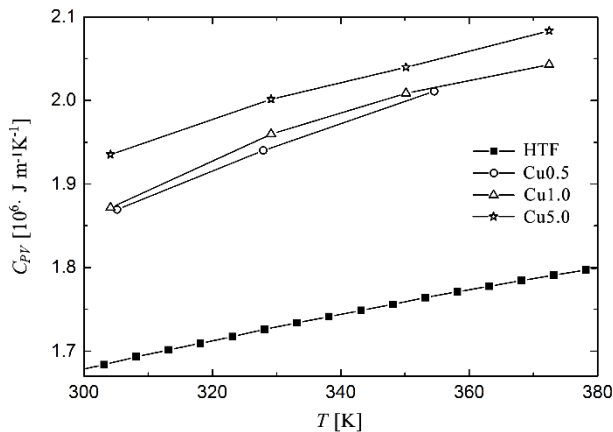


Figure 5 Volumetric heat capacity values for the nanofluids prepared with respect to temperature. The values for the base fluid reported by the supplier are included for comparison purposes.

Viscosity

The dynamic viscosity of the HTF is one of the parameters that affect to the heat transfer performance, as discussed above. Moreover, it affects to important features as the pumping power or possible drops in pressure. So, the dynamic viscosity of the nanofluids prepared was measured at around room temperature in order to use values of the properties in the Dittus-Boelter correlation measured at near temperatures. Also, viscosity of the base fluid was measured following the same procedure in order

to check the methodology used. The deviation with respect of the value provided by the supplier was around 1%.

Thus, Figure 6 shows the value of the dynamic viscosity obtained with respect to the nanoparticle mass fraction, ϕ . As expected, an increase of the viscosity is observed for the nanofluids with respect to the base fluid. This increase was up to 7.9%. This increase is usual in this kind of system due to the low nanoparticle size used that is the lower nanoparticle size the higher viscosity [20]. The presence of a large number of nanoparticles invoke a greater interaction between them, which causes an increase of the resistance to flow, that is in the viscosity [21]. Moreover, an increase of the viscosity was observed when the nanoparticle mass fraction increased, which is coherent with results reported in the literature [22]. An increase of the number of nanoparticles provoke an increase of the interaction between them, and therefore of the viscosity [21]. Finally, the viscosity did not follow a linear trend with respect to the nanoparticle mass fraction, as with density. This is a typical behaviour when the nanoparticles interact between them and the internal morphology of the system is changing. So, the increase of the concentration can produce agglomerations of the nanoparticles and therefore can change the trend of the viscosity.

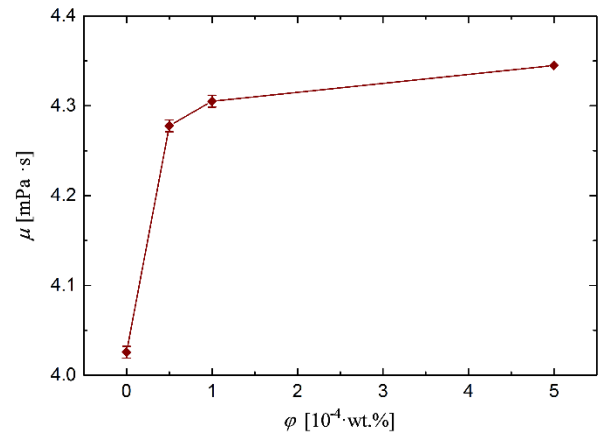


Figure 6 Dynamic viscosity values for the nanofluids prepared with respect to Cu nanoparticles mass fraction, ϕ .

Performance of the nanofluids

The evaluation of the performance of the nanofluids prepared was developed according to the Dittus-Boelter correlation, as is discussed above, using the equation (1). For this reason, the values of the density, thermal conductivity, heat capacity and viscosity have been determined. From these values, the ratio for the heat transfer coefficient were calculated at room temperature. The value of 1 for this ratio is correlated with the behaviour of the base fluid. In turn, a values higher than 1 implies an enhancement of the heat transfer performance.

Figure 7 shows the values of the ratio of the heat transfer coefficient with respect of the Cu nanoparticle mass fraction, ϕ . It is possible to observe that the efficiency of the system is improved up to 11% thanks to the incorporation of Cu nanoparticles into the base fluid.

CONCLUSION

In this work, the performance of nanofluids based on Cu nanoparticles and a eutectic mixture of diphenyl oxide and biphenyl as the base fluid has been analysed. This base fluid is used as a heat transfer fluid in Concentrating Solar Power plants.

The analysis of the performance of the nanofluid has been developed using the Dittus-Boelter correlation. Thus, density, dynamic viscosity, thermal conductivity and heat capacity have been estimated and analysed. The nanofluids showed a slight increase of the density because the Cu nanoparticle mass fraction is low. Also, dynamic viscosity is observed to increase up to 7.9% for the most concentrated nanofluid. Moreover, the thermal conductivity increased up to 13%. In turn, the evolution of thermal conductivity with respect to temperature is similar to that for the base fluid, that is the higher temperature the lower thermal conductivity. Finally, heat capacity is observed to increase for the nanofluids prepared up to 14%. In turn, the volumetric heat capacity increased according to the increase of the heat capacity, about 15%.

So, in this work we have introduced the possible use of this nanofluid system in CSP plants. Further research at high temperatures is under development.

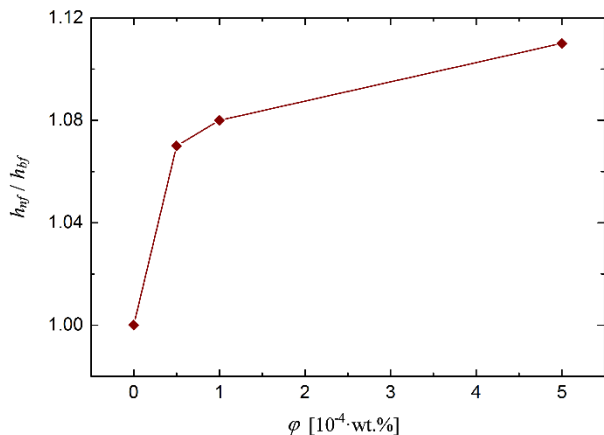


Figure 7 Values of the ratio of the heat transfer coefficient for the nanofluids prepared with respect to the base fluid at room temperature.

Therefore, from these values, the performance of the nanofluids prepared, evaluates as the ratio of the heat transfer coefficient according to Dittus-Boelter correlation, increased up to 11% with respect to the base fluid.

ACKNOWLEDGEMENTS

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Comments to the reviewers

At first time, we would like to indicate our grateful for the comments of the referees. Next, we expose comments (in blue) to the report.

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Review 1
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> *** Recommendation: Please motivate the above (acceptance, minor revision, major revision or reject). A short motivation is mandatory.

work has been described in a brief but concise way. It might be given the more graphics.

Answer: Thanks for reviewing our manuscript.

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Review 2
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> *** Recommendation: Please motivate the above (acceptance, minor revision, major revision or reject). A short motivation is mandatory.

The authors prepared nanofluids using commercial materials: Cu nanoparticles and eutectic mixture of diphenyl oxide and biphenyl. They spent large effort to characterize the different properties such as density, viscosity, heat capacity, and thermal conductivity. Then they found out the nanofluids have improved heat transfer performance up to 11% according to the Dittus-Boelter correlation. This manuscript is well-written and concise. However, the manuscript didn't show enough novelty and details and it has severe issues in stating the motivation of the work. Therefore, the reviewer doesn't recommend this manuscript in its current stage to be accepted as a HEFAT2016 proceeding paper, unless the authors address the following comments properly.

> *** Corrections: Please list mandatory corrections that should be considered in this section.

1. The authors claimed their main motivation of this study is the analysis of the nanofluids which can be used in high temperature applications like HTF in concentrating solar power plants. However, the temperature range studied (300-380 K) is far less than the working temperature of the HTF in CSP plants (> 650 K). In this working temperature, there are only few HTFs are applicable, like oil or molten salt. Thus, the authors need to find other meanings for the current work. The title should also be modified accordingly. Otherwise, the measurement has to go to much higher temperatures.

Answer: The base fluid used in this work is the eutectic mixture of diphenyl oxide and biphenyl. This fluid is typical in Concentrating Solar Power plants, that is it is one of the few HTF applicable in this technology. Authors of this work know several plants where this fluid is really used. For this, the use of the nanofluids prepared in this work is focused for its use in CSP at high temperature. In turn, the nanofluids have been compared with the base fluid in several properties and the comparison has been done at a few temperatures, but this research is included in a complete research project and the study of the nanofluids prepared follow. So, we show results with these nanofluids that we think they are very interesting because we show a probably improve in the efficiency of the heat transfer process. So, further research at high temperature is under development. But the results reported in this manuscript are very interesting.

2. The reviewer didn't see any meaning of Figure 1. Please explain or remove it.

Answer: This figure is interesting because it is possible to observe the properties of the base fluid. From these properties it is possible to understand why this fluid is used in high temperature applications. For example, the low vapour pressure or high heat capacity are good reasons. In the manuscript some of these properties are compared with the properties of the nanofluids, and we can observe how the differences are slight and the performance as heat transfer fluid is improved, and therefore, these results make us to think that the nanofluids can be used as HTF in high temperature applications. So, the interest of this figure has been clarified in the manuscript.

3. What is the purpose of measuring specific heat, heat capacity and thermal conductivity at different temperatures when only showing one temperature viscosity and performance at the end? The temperature dependence trends also didn't show interesting phenomena. The concentration dependence would be more interesting.

Answer: It is possible to observe how the trend for heat capacity and thermal conductivity is the same than for the base fluid. This is the reason of measuring at different temperatures. Moreover, the concentration dependence is observed for thermal conductivity and for heat capacity in Figures 3 and 4, respectively.

4. Why the density and viscosity didn't follow a linear trend along the nanoparticle mass fraction? Are they supposed to? Why the trends are very similar for density and dynamic viscosity? Please explain the connection. It also seems that there is a transition point around the second point, please explain if it is related to some theory like shear thinning or thickening. More data points for mass fraction especially between the first two points would make the result more solid and convincing. The transition stage would be clearer and more meaningful for understanding the behind mechanism.

Answer: This behaviour for density and viscosity is typical for this kind of systems. Both properties depends on the nanoparticle size and the nanoparticle size can depend on the concentration due to process of agglomeration of nanoparticles. The size of the agglomerated nanoparticles set changes with the concentration. As we exposed in the manuscript (page 2) this is due to the interaction between nanoparticles. Probably this interaction can produce some process like shear thinning or thickening as reviewer suggested, but it is not easy to know which process is. More research in this field is necessary. Thanks for this comment to reviewer, we will work on this topic. We have included a brief new discussion about this in the manuscript.

5. What temperature is the measurement at in Fig. 6? Why not showing all data from different temperatures for comparison and revealing more insight of the high temperature effect?

Answer: This measurement was performed at about room temperature in order to compare with the values of the other properties in the Dittus-Boelter correlation. This has been clarified in the manuscript.

6. Comparison with literature on Cu nanoparticle nanofluids at low temperature for the heat transfer performance would be appreciable. The reader would also have better overview and realize the contribution of this work.

Answer: The typical application for low temperature uses other fluids as the base fluid of the nanofluid, such as water or ethylene glycol. In our case, the base fluid used is a eutectic mixture of diphenil oxide and byphenil, and nanofluids with so different base fluid cannot be compared. The nature of these fluids is very different and therefore the interactions between nanoparticles and fluids will be very different. It is noteworthy that the internal interactions between nanoparticles and fluid will be the responsible of all properties of the nanofluids. On the other hand, the study of nanofluids based on base fluid like the one used in this work is not usual in the literature and only a few papers are found and the results are difficult to compare. For this reason, much research in this filed is necessary and for this we are working in this topic, and our research of these nanofluids is under development.

7. What does the increase of 11% for the performance really mean? It is better to check some reference from government agency that what performance corresponds to how much saving of energy or money.

Answer: As is explained in the manuscript, this is the increase of the heat transfer coefficient (h).

> *** Originality: How novel and innovative is the paper? A paper presenting methods or application domains not frequently discussed will receive a high mark. This also takes into consideration whether the topic has been published in similar form before. If the paper contains mostly known material, i.e. established methods and well understood application domains, it is not considered very original. Empirical case studies of a particular application domain are often highly original, but may have only limited significance to the field.

Marginal (1)

Answer: As exposed above, there is a few studies in the literate about nanofluids based on the base fluid used in this work, and this is a field under development at the moment. Probably, if we make a nanofluid using Cu nanoparticles and water, the originality will be Marginal. But using this fluid, I disagree.

> *** Significance: Does the paper make a valuable contribution to the theory or the practice of heat transfer, fluid mechanics and/or thermodynamics? A high significance indicates a high influence of this research on following publications in the field or applications, implications for practices, policies and future research etc. It represents an indicator of the importance of the findings, regardless of their degree of originality.

Not significant (0)

Answer: I disagree. Again, there is a few papers using this kind of base fluid. And as exposed above, this base fluid is really used in operative CSP plants in Europe.

> *** Content: What is the information content of the paper? Does the paper allow non-experts in the field to comprehend its research objective?

Good (3)

> *** Soundness: Is the paper technically correct (considering its submission category)? What is the technical quality?

Acceptable (2)

> *** Clarity: Is the paper well presented and organised? A well presented paper enhances the understanding of the presented content also to non experts in the field. It often shows clear and logical presentation, appropriate style, the standard of English, freedom from errors, ease of reading, correct grammar and spelling, appropriate abstract, adequate use of graphical materials and tables to support ideas & findings, conformance with format for referencing, length and format details. HEFAT is an international conference, so English quality may be substandard. Please indicate mandatory revisions and the need for corrections through a native English speaker, if the content of the paper is still comprehensible. Indicate it if the level of English prohibits an understanding of the thoughts presented.

Very clear (3)

> *** Relevance: Is the content/topic of the paper relevant to the conference theme of heat transfer, fluid mechanics and thermodynamics?. Answer Yes or No please.

Yes (1)

> *** Comments (optional): Any other comments that the reviewer wants to make?