Procedia
Environmental Science,
Engineering and Management
http://www.procedia-esem.eu

Procedia Environmental Science, Engineering and Management **8** (2021) (1) 147-155

Environmental Innovations: Advances in Engineering, Technology and Management,
EIAETM, 19th-23rd October, 2020

THERMAL PROPERTIES OF HITEC SALT-BASED NANOFLUIDS SYNTHESIZED BY NEW TWO-STEP METHOD*

Marllory Isaza-Ruiz, Francisco Bolívar Osorio**

Centro de Investigación, Innovación y Desarrollo de Materiales CIDEMAT, Facultad de Ingeniería, Universidad de Antioquia UdeA, Calle 70 No. 52-21, Medellín, Colombia

Abstract

The use of molten salt-based nanofluids as a thermal storage medium, the evaluation of their thermophysical properties, and the development of new more efficient synthesis methods, have attracted great interest from researchers. In this way, this work focuses on the development of a new two-step method in which the use of water in the process is eliminated, without affecting the stability and homogeneity of the particles within the salt. Molten salt-based nanofluids with Hitec as base fluid and alumina nanoparticles as an additive in three different proportions 0.5, 1.0, and 1.5 wt% with a 13.6 nm nominal size. The thermal properties, melting point, specific heat capacity, and thermal stability were evaluated, as well as, the microstructural analysis to determine the good distribution of the nanoparticles in the salt. The increase of up to 14.6% of the specific heat of the molten salt-based nanofluids compared to the base salt, as well as the decrease in the melting point without affecting the thermal stability demonstrate the viability of the proposed method for the synthesis of nanofluids for thermal energy storage in CSP plants.

Keywords: CSP, hitec, molten salt, nanofluids, thermal properties

1. Introduction

New renewable sources are being highly researched and implemented as a way to mitigate large amounts of greenhouse gases, as well as to meet global energy demand without using traditional fossil-based energy sources. Concentrated solar power energy (CSP) stands out as a promising renewable source with an annual production of 5.5 GW in

* Selection and peer-review under responsibility of the EIAETM
** Corresponding author: e-mail: marllory.isazar@udea.edu.co

2018. The carbon footprint during its life cycle is lower than the one of fossil fuels, with a worldwide annual reduction in GHG emissions of approximately 7.54 Mt. The Thermal Energy Storage System (TES) with molten salts can improve the mitigations of the CSP plants, thanks to the electricity generation even in the absence of sunlight, avoiding the consumption of the fossil fuels.

Implementing molten salt into CSP allows lower Levelized cost of energy (LCOE). However, molten salts commonly used in the TES has low thermal properties, specific heat capacity typically less than 2 J / (g°C) and thermal conductivity less than ~1 W / (m K). For that reason, several types of researches have been made in order to improve these fluids, within which is the development and implementation of the molten salt-based nanofluids (MSBNFs), a stable colloidal suspension of nanomaterials with average sizes < 100 nm in the molten salt.

The use of nanofluids based on molten salts is being highly investigated thanks to its outstanding thermophysical properties compared to the base salt. Usually, the most common method for its synthesis has a significant amount of water as its dispersion medium, so some research focuses on the development of new methods with which water is avoided or eliminated from the process, without affecting its thermal properties and increasing as far as possible the stability and homogeneity of the nanoparticles within the salt. Chieruzzi et al. (Chieruzzi et al., 2017) evaluated the mixtures of 1 wt. % of Silica (SiO_2), alumina (Al_2O_3), or both (SiO_2-Al_2O_3), with Solar Salt directly, at high temperature, using a twin-screw micro-compounder. They obtained an increment of the specific heat capacity of up to 18.6% with 1 wt. % of SiO_2-Al_2O_3. Navarrete et al. (Navarrete et al., 2020) evaluate different nanofluid synthesis methods including the ball mill dry method and a spray drying method proposed. Nevertheless, none of these reports used the commercial salt Hitec as a base salt.

Hence, this study presents a new alternative two-step method in order to ensure a homogeneous and colloidal suspension of the nanoparticles before mixing with the molten salt, avoiding the use of water in the process. For this, the commercial salt Hitec (53% KNO_3-40% $NaNO_2$-7% $NaNO_3$, mol. %) was used as the base fluid, along with 0.5, 1.0, and 1.5% by weight alumina nanoparticles (Al_2O_3) with nominal size of 13.6 nm, in order to obtain the MSBNFs. The thermal characterization, specific heat capacity evaluated by Modulated Differential Scanning Calorimetry, the melting point for Differential Scanning Calorimetry and the thermal decomposition obtained by Thermogravimetric analysis are presented, as well as the microstructural analysis by SEM after the thermal evaluation to ensure the presence of the nanoparticles inside the samples evaluated and their homogeneity

The main objective of this study is to analyze the thermal properties of the molten salt-based nanofluids with Hitec as base fluid and alumina nanoparticle as an additive in three different proportions, 0.5, 1.0 and 1.5 wt%, synthesized by a new two-step method in order to avoid the use of water in the process and decrease the time of the synthesis. Demonstrating the feasibility of the proposed method thanks to the good thermal properties obtained.

This work is divided into two main parts:

- Synthesis of the molten salt-based nanofluids by a new two-step method using Hitec as base fluid and alumina nanoparticle as an additive avoiding the use of the water in the process.
- Evaluation of the thermal properties, melting point, specific heat capacity, thermal stability as well as the microstructural analysis to determine the feasibility of the proposed method to synthesized molten salt-based nanofluids for use as a thermal storage medium in CSP plants.

2. Materials and methods

2.1. Preparation of the molten salt

The salt mixture was prepared in the laboratory from pure high-grade chemicals according to the known formulations Hitec (7 wt. % $NaNO_3$-53 wt. % KNO_3-40 wt. % $NaNO_2$). The nitrite and nitrate salts used were $NaNO_2$, $NaNO_3$, and KNO_3 (98 %) Reagent Grade purchased from Merck. Pure salts contain different levels of impurities, primarily consisting of chloride, magnesium, and sulfate. The level of impurities in the salts according to the salt provider is given in Table 1.

In the beginning, the salt mixtures were carefully prepared in an agate mortar for around 20 min under atmospheric conditions according to the proportion described above. After that, the mixture was heated in a Nabertherm LT 9/12/P330 muffle furnace until the melting point (~160°C) in a quartz vessel for around 1 h, and the temperature was raised to 270°C for 48 h to eliminate the presence of moisture. Later, the mixture was cooled faster in a stainless steel container submerged in cold water, distributing it homogeneously at the bottom in such a way that there was a layer of ca. 5 mm thick, fast cooling it until the salt was completely solid.

2.2. The proposed new method: Traditional Method with Modification

The method used to elaborate the molten salt-based nanofluids was a traditional method with modification, by using butanol instead of water, with the aim to ensure a homogeneous and colloidal suspension of the nanoparticles before mixing with the molten salt. Considering that the alumina nanoparticles form stable suspensions in slightly polar solvents as 1- butanol. Consider that the alumina nanoparticles form stable suspensions in slightly polar solvents as 1-butanol, ensuring the homogeneous suspension of the nanoparticles first in the butanol, it is ensuring the homogeneous suspension of the nanoparticles first in the butanol, it is possible to obtain a homogeneous distribution of them after the addition of the molten salt. Once the salt is obtained by the procedure established above, the mixture was homogenized using an agate mortar for 15 minutes. The homogeneous powder was mixed with the nanoparticles (0.5, 1.0, and 1.5 wt.%), which were previously mixed with 10ml of butanol, and forming a stable suspension sonicated continuously for at least 1 hour. After that, the mixture was subjected to a cycling process between 160 and 270°C at least 2 times, and fast cooling in a stainless steel container submerged in cold water to ensure the structure of the salt in the molten state and not allow time for the formation of new structures.

Table 1. The reported level of impurities in the nitrate/nitrite salts.

Pure salt	*Amount (wt. %)*				
	Chloride (Cl^-)	*Magnesium (Mg^{2+})*	*Sulfate (SO_4^{2-})*	*Insoluble*	*Moisture*
$NaNO_2$	<0.01	<0.01	0.01	<0.025	<0.05
$NaNO_3$	<0.05	<0.005	<0.01	<0.025	0.1
KNO_3	<0.002	<0.005	<0.01	<0.025	0.05

2.3. Thermophysical Properties Determination

2.3.1. Transmission electron microscopy TEM

The size and shape of alumina nanoparticles used to elaborated the MSBNF were observed by electron transmission microscope, TEM (Tecnai F20 Super Twin TMP), using a source of emission of fields, resolution of 0.1 nm in 200 Kv. Taking into account the low solubility of alumina in butanol, the particles were dispersed in it, then an aliquot was placed on a copper grid (Lacey carbon mesh 200) and heated long enough to ensure the solvent elimination.

2.3.2. Scanning Electron Microscopy (SEM)

The samples were fixed on a graphite tape, covered with a thin gold coating (DENTON VACUUM Desk IV equipment) and analyzed in the high vacuum scanning electron microscope (JEOL JSM 6490 LV) to obtain high-resolution images. The detector of secondary electrons was used to evaluate the morphology and topography of the samples. The elemental analysis was carried out by energy-dispersive X-ray spectroscopy EDS (reference INCA PentaFETx3 Oxford Instruments). SEM images were carried out after the MDSC measurement to verify the presence of the nanoparticles inside of the molten salt as well as to evaluate the agglomeration.

2.3.3. Differential Scanning Calorimetry

The melting point was measured using a differential scanning calorimetry (DSC; Q200, TA Instrument, Inc.). Tzero hermetic pan/lid aluminum (TA instruments) was used to place the samples in the DSC and analyzed by TA Universal Analyzer 2000 version 4.5A. The sample mass was around 10 mg for all samples. The thermal cycle was realized in a nitrogen atmosphere, starting at room temperature until 400°C at a rate of 10 °C / min, followed by equilibration at 40°C. The test had a sampling interval of 0.10 s / pt, and 2 cycles were realized to obtain a homogeneous result. The melting temperature of the sample was taken as the main endothermic peak in the DSC curve.

2.3.4. Modulated Differential Scanning Calorimetry

Modulated differential scanning calorimeter (MDSC; Q200, TA Instrument, Inc.) was used to estimate the specific heat capacity of the samples, using aluminum crucibles and N_2 atmosphere. The samples were heated up to 250°C and held at this temperature for 5 min to obtain a stable heat flux signal, after that, the applied amplitude was ± 0.50 °C every 130 s, and finally was heated again until 350 °C at 2 °C / min. The specific heat capacity was reported for both methods at 300 °C, since this is the temperature at which the salt in Parabolic Trough Plants is commonly maintained. The reference used was standard sapphire. Several factors can influence the results of the measurement, including heating rate and sample size. For that reason, it was established that 10 mg of sample was the adequate weight to obtain homogeneous and reproducible results. Peak analysis was performed using the Universal Analysis 2000 version 4.5A. These procedures were applied to measure the specific heat capacity of every sample, pure samples, and mixtures.

2.3.5. Thermogravimetric Analysis

The thermal stability of pure Hitec and the MSBNFs were determined by thermogravimetric analysis (TGA; Q500, TA Instrument, Inc.) under a constant stream of nitrogen at a flow rate of 50 ml/min, temperature ramp of 15°C / min in the range 25-800 °C and isothermal for 5 min.

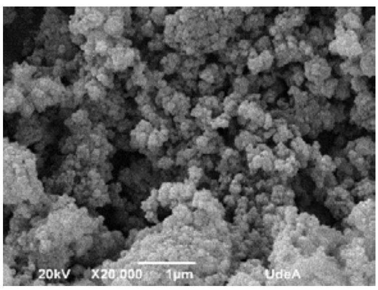
3. Results and discussion

3.1. Morphology of Alumina

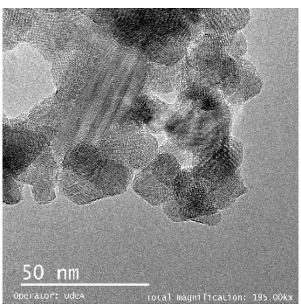
Fig. 1 a and b shows the SEM and TEM images of the pristine alumina nanoparticles used to elaborate the MSBNFs, respectively, as well as, Fig. 1 c the size distribution with an average size of 13.6 nm which is even smaller than that reported by the supplier of 40 nm. The regular shape can be observed in the SEM and TEM images, as well as the presence of agglomerates, which can be eliminated or reduced during the MSBNFs synthesis process, as well as the shape of the alumina is characteristic of alpha alumina.

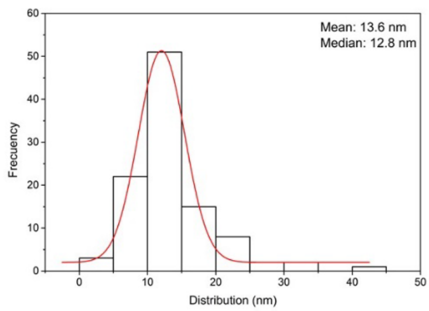
3.2. Melting Temperature (Tm)

The melting temperature values of the pure Hitec and the MSBNFs were obtained by DSC. Two heating and cooling runs have been carried out to avoid discrepancies in the melting temperature produced by the hygroscopic property of some nitrates. The first cycle has been made to achieve the perfect mixing of the mixture, and the results from this sequence have never been taken into account. The other cycle was analyzed, and the data from these runs are reported Table 2. Given that both the base molten salt (Hitec) and the nanofluids with the different proportions of the alumina nanoparticles are not pure materials, and considering the previous reports made by Gimenez and Fereres (Gimenez and Fereres, 2015) et Mohammad et al. (Mohammad et al., 2017), the heating rate affects the onset of melting as well as the peaks height, peaks width, and transition enthalpies.



a.





b. c.

Fig. 1. The pristine alumina nanoparticles used to elaborate the MSBNFs. a. SEM image, b. TEM image and c. the size distribution obtained from TEM images

Therefore, the melting temperature of the sample is taken as the endset temperature of the main endothermic peak at the DSC curve.

Thereby, the melting point correspondent to the Hitec salt was 145.38°C and the endset point was obtained at 149.83°C, slightly higher than reported in the literature (Moyer, n.d.). This behavior may be related to the preparation of salt in the laboratory without atmospheric control during the fusion process, that is, the fusion was performed under an air atmosphere. As indicated by Olivares (Olivares, 2012) the use of air during fusion can change the composition of the initial mixture after oxidizing part of the nitrite to nitrate raising the melting point.

The addition of Alumina leads to an apparent reduction of the onset, endset, and melting point temperature. This effect was found for all samples investigated, but it was more evident for the MSBNF with 1.0 wt.% of nanoparticles compared to the base salt, up to 4.93 %. This behavior corresponds to the reports of several authors (Chieruzzi et al., 2013) in which the thermal properties of the molten salt have higher enhancement with 1.0 wt.% of Al_2O_3, and with a greater amount of nanoparticles the thermal properties begin to be affected negatively. In particular, the onset temperature decreased by adding Al_2O_3. This performance means that the phase change occurs at a lower temperature in comparison to the base salt; this behavior is a clear advantage for use in CSP plants.

3.3. Specific Heat Capacity (Cp)

The specific heat capacity was measured using modulated differential scanning calorimetry (MDSC) in a temperature range 250 to 350°C, considering the normal operating temperature in CPS plants, especially parabolic through collectors, only results are reported at 300°C. Hence, Table 3 shows the Cp of the pure Hitec and the MSBNFs synthesized by the new two-step method.

The results show a positive effect in all the samples after the addition of the alumina nanoparticles in different concentrations, an apparent improvement in Cp up to 14.08 % with the addition of 1.5 wt.% of Al_2O_3 was evident, this result together with the reduction of the melting point demonstrate that new method is viable for the manufacture of molten salt-based nanofluids for thermal storage applications in CSP plants, avoiding the use of water in the process and therefore its subsequent elimination.

Table 2. The melting point of pure Hitec and MSBNFs.

Sample	***Melting Point (°C)***	***Change Percentage (%)***	***Standard Deviation (SD)***	***Onset (°C)***	***Endset (°C)***	***Heat of Fusion (J/g)***
Hitec (H)	145.38	-	0.53	139.36	149.83	85.43
H+0.5% Al_2O_3	138.98	-4.40	1.41	128.62	144.99	70.40
H+1.0% Al_2O_3	138.71	-4.93	0.25	127.42	144.50	68.42
H+1.5% Al_2O_3	139.27	-4.21	0.69	131.75	145.57	77.07

Table 3. Average specific heat capacity of pure Hitec and the MSBNFs.

Sample	***Specific heat capacity (J/g°C)***	***Change Percentage (%)***	***SD***
Hitec (H)	1.46	-	0.033
H+0.5% Al_2O_3	1.67	14.63	0.143
H+1.0% Al_2O_3	1.60	9.66	0.011
H+1.5% Al_2O_3	1.67	14.08	0.001

According to the standard deviations, there was no statistically significant difference between the evaluated samples, which would indicate a similar increment of Cp of the MSBNFs with 0.5 and 1.0 wt.%.

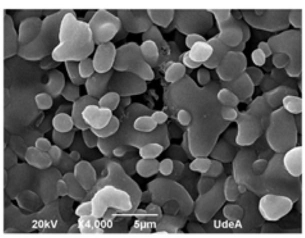
3.4. Microstructural Analysis

To determine the presence of the nanoparticles after the measurement of the Cp by MDSC, as well as to observe the degree of dispersion and agglomeration of solid particles in the molten salt, the microstructural study was carried out using Scanning Electron Microscopy (SEM). Fig. 2 a. shows the SEM image of the pure Hitec and the nanofluids b, c, and d correspond to the proportions 0.5, 1.0, and 1.5 wt.% of alumina respectively. The presence of the alumina nanoparticles in all samples prepared was evident, as well as the uniform nanoparticle dispersions inside the molten salt that can be observed for all samples evaluated. It is important to highlight that this research did not show the presence of the interconnecting network of nanoparticles or needle-like structure as reported for some authors (Shin and Banerjee, 2011). However, the not presence of these connecting networks has been reported by several authors (Chieruzzi et al., 2017). Therefore, this is not the reason why there is a significant increase in Cp, although the distribution in the solid-state does not necessarily correspond to the distribution of the nanoparticles in the molten state. In this case, the increment of the heat capacity could be due to the high surface area of the nanoparticles per unit volume and the particle size distribution, that is, smaller particles may be more dispersed within the salt and increase thermal properties (Chieruzzi et al., 2013).

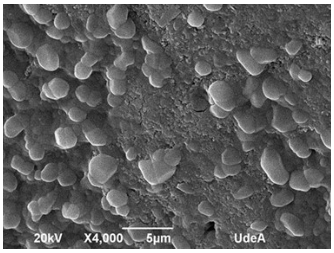
3.5. Thermal Stability

The results for the TGA experiments are summarized in Table 4, to evaluate the thermal stability both the molten salt Hitec and the MSBNFs with 0.5, 1.0 and 1.5 wt.% of alumina nanoparticles synthesized by the new two-step method, the criterion for the maximum stability temperature where 3 % of overall weight has been lost, was followed a temperature of 300°C was chosen as the initial temperature where the mass loss started.

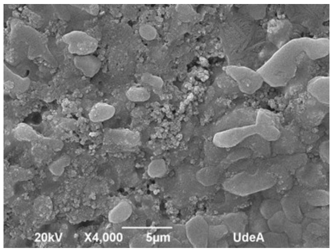
Hitec and the nanofluids present a similar decomposition curve and the thermal stability under N_2 atmosphere of Hitec was 621.88°C, this value is slightly below that reported by some authors such as Villada et al. (Villada et al., 2019) who reported a decomposition temperature value of 639.11°C and Fernández et al. (Fernández et al., 2015) informed 630.97°C, both in an inert atmosphere. However, in the literature are presented a thermal stability range between 535 to 538°C under N_2 atmosphere and 610°C under the same atmosphere, this behavior may be due to both the raw materials and the salt preparation method, showing that there is not a consensus about this thermal property. On the other hand, for the MSBNFs the decomposition temperature was higher than 616°C, it was not significantly affected by the addition of the nanoparticles. In the same way, according to the bulk decomposition values were also not significantly affected by the addition of nanoparticles, and the Hitec result is close to that reported by other authors (Olivares, 2012).



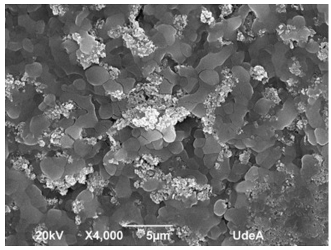
a.



b.



c.



d.

Fig. 2. SEM images of a. Pure Hitec, b,c, and, d the MSBNFs after MDSC with 0.5, 1.0, and 1.5 wt.% of alumina nanoparticles, respectively.

Table 4. Thermal stability analysis under N_2 of pure Hitec and MSBNFs

Sample	***Thermal decomposition (°C)***	***SD***	***Change Percentage (%)***	***Bulk of decomposition (°C)***	***SD***	***Change Percentage (%)***
Hitec (H)	621.88	0.58	-	785.68	4.58	-
H+0.5% Al_2O_3	620.97	4.14	-0.15	784.92	9.57	-0.10
H+1.0% Al_2O_3	617.60	5.49	-0.69	790.18	2.83	0.57
H+1.5%Al_2O_3	631.75	6.99	1.59	790.67	1.34	0.64

4. Conclusions

A new method of synthesis of Hitec salt-based nanofluids by two-steps was presented, its main advantages being the elimination of water and the reduction of process time. The good thermal properties obtained, higher specific heat compared to the base salt, a lower melting point and good thermal stability show not only the improvement in the thermal properties of the salt but also the feasibility of using the proposed method for the synthesis of nanofluids with potential application in thermal energy storage systems in CSP plants, contributing to the improvement of the system efficiency and to the reduction of greenhouse gas emissions.

Acknowledgments

The authors, particularly Marllory Isaza-Ruiz, are grateful for the financial support provided by the Doctoral Grant number 727-2015 funded by “Departamento Administrativo de Ciencia, Tecnología e Innovación-COLCIENCIAS”

References

Chieruzzi M., Cerritelli G.F., Miliozzi A., Kenny J.M., (2013), Effect of nanoparticles on heat capacity of nanofluids based on molten salts as PCM for thermal energy storage, *Nanoscale Research Letters*, **8**, 448.

Chieruzzi M., Cerritelli G.F., Miliozzi A., Kenny J.M., Torre L., (2017), Heat capacity of nanofluids for solar energy storage produced by dispersing oxide nanoparticles in nitrate salt mixture directly at high temperature, *Solar Energy Materials and Solar Cells*, **167**, 60-69.

Fernández A.G., Galleguillos H., Fuentealba E., Pérez F.J., (2015), Thermal characterization of HITEC molten salt for energy storage in solar linear concentrated technology, *Journal of Thermal Analysis and Calorimetry*, **122**, 3-9.

Gimenez P., Fereres S., (2015), Effect of heating rates and composition on the thermal decomposition of nitrate based molten salts, *International Conference on Concentrating Solar Power and Chemical Energy Systems, SolarPACES 2014*, **69**, 654-662.

Mohammad M.B., Brooks G.A., Rhamdhani M.A., (2017), Thermal analysis of molten ternary lithium-sodium-potassium nitrates, *Renewable Energy*, **104**, 76-87.

Moyer D., n.d., *Coastal Hitec Heat Transfer Salt*, Coastal Chemical Co., L.L.C., On line at: http://www.skyscrubber.com/MSR%20-%20HITEC%20Heat%20Transfer%20Salt.pdf.

Navarrete N., Hernández L., Vela A., Mondragón R., (2020), Influence of the production method on the thermophysical properties of high temperature molten salt-based nanofluids, *Journal of Molecular Liquids*, **302**, 112570.

Olivares R.I., (2012), The thermal stability of molten nitrite/nitrates salt for solar thermal energy storage in different atmospheres, *Solar Energy*, **86**, 2576-2583.

Shin D., Banerjee D., (2011), Enhancement of specific heat capacity of high-temperature silica-nanofluids synthesized in alkali chloride salt eutectics for solar thermal-energy storage applications, *International Journal of Heat and Mass Transfer*, **54**, 1064-1070.

Villada C., Jaramillo F., Castaño J.G., Echeverría F., Bolívar F., (2019), Design and development of nitrate-nitrite based molten salts for concentrating solar power applications, *Solar Energy*, **188**, 291-299.