THERMOPHYSICAL PROPERTIES OF A NANOFLUID BASED ON A EUTECTIC MIXTURE OF DIPHENY AND DIPHENYL OXIDE AND CARBON BLACK NANOPARTICLES

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ABSTRACT

Synthetic thermal oils are used as heat transfer fluids (HTFs) in different applications, due to their higher working temperature. In this way, one of the applications of interest is the use of thermal oils in Concentrated Solar Power (CSP) plants with Parabolic Trough technology. Nowadays, the HTF known commercially as Therminol VP1 (Solutia Inc.) is being used in CSP plants. This fluid is composed of a eutectic mixture of diphenyl ($C_{12}H_{10}$) and diphenyl oxide ($C_{12}H_{10}O$), and it is used as an HTF with a maximum working temperature of 400ºC. However, one of the drawbacks of Therminol VP1 is its low thermal conductivity. In recent years it has been demonstrated that the addition of nanoparticles can improve the thermal properties of HTFs, and they are then called nanofluids. The key factor of nanofluids is their high stability over time, understanding stability of a nanofluid as its capacity of keeping low agglomeration and sedimentation rates of nanoparticles. However, at high temperatures it is necessary to add chemically compatible surfactants that do not degrade and endow the nanofluids with stability through steric repulsion even under high temperature conditions. In this work, a carbon black/Therminol VP1 nanofluid was synthesized and stabilized using diphenyl sulfone as a stabilizer. Stability tests after thermal cycling at 400ºC showed the higher performance of this additive compared to others commonly used in the literature. Thermal conductivity, and heat capacity of the nanofluids at 3 vol% and 5 vol% were characterized from 50ºC to 350ºC.

NOMENCLATURE

List of abbreviations

CSP	Concentrated Solar Power
CB	Carbon Black
DSC	Differential Scanning Calorimetry
SDS	Sodium dodecyl sulfate
SDBS	Sodium dodecylbenzenesulfate
DS	Diphenyl sulfone
HTF	Heat Transfer Fluid

Special characters

C_p	[J/Kg]	Specific heat
k_n	[W/m·K]	Thermal conductivity
ϕ	[-]	Volume fraction
ρ	[Kg/m^3]	Density
d_p	[nm]	Particle diameter

Subscripts

bf	Base fluid
nf	Nanofluid
np	Nanoparticle

INTRODUCTION

The most widely used heat transfer fluids (HTFs) for medium and high working temperature applications are thermal oils. These applications include chemical production, pharmaceuticals manufacturing, oil and gas processing or Concentrated Solar Power (CSP) plants.

Attending to their composition, different types of thermal oils can be described. Synthetic thermal oils present low viscosity and high stability for high working temperature conditions, which makes them widely used for processes with operating temperatures between -80ºC and 365/400ºC.

Therminol VP1, brand name for the synthetic thermal oil consisting of an eutectic mixture of diphenyl oxide and diphenyl (73.5%-26.5% respectively), is widely used in CSP plants, given its great stability for continuous bulk operation temperatures up to 400ºC. This is an important feature for HTFs, as the efficiency of the solar plant depends directly on its maximum working temperature. However, the main drawback of thermal oils is their low thermal conductivity, which limits their performance as heat transfer fluids.

A nanofluid is an engineered colloidal suspension of nanometric sized particles. This concept was firstly proposed by M. Masuda [1] and S.U.S. Choi [2]. In nanofluids, solid particles, if properly dispersed, move inside the liquid because of its Brownian motion due to their reduced particle size. Therefore, if nanoparticle agglomeration is avoided after collisions, no sedimentation will exist, leading to a stable nanofluid that will present, to some extent, the liquid transport properties, while adding, also to some extent, physical properties inherent to the solid.

Extensive research about the use of nanofluids as HTFs with enhanced thermal properties has taken place over the last two decades [3-6]. In order to create stable nanofluids, e.g. with low agglomeration rates to avoid clustering and sedimentation of nanoparticles over time, stabilizers may be added to the suspension. In non-aqueous media, agglomeration is avoided through steric repulsion surfactants.

For thermal applications, one of the main benefits of nanofluids is the increase of their thermal conductivity compared to that of the base fluid. On the other hand, their main disadvantage is the higher dynamic viscosity values due to the solid particles. Besides, special care must be taken reagarding stability, as it is critical for their practical application. More detailed information about stability issues in nanofluids can be found in [7].

Up to date, the great majority of the works published about synthetic thermal oils-based nanofluid uses aromatic-based oils [8, 9-12]. However, very few studies using Therminol VP1 as a base fluid have been published [13-16].

Regarding the solid nanoparticles used, carbon has been used as an enhancer for the base fluid properties in previous research [16-18]. High chemical stability exhibited by carbon nanoparticles with most chemical compounds makes them convenient for their use with Therminol VP1, whose two main compounds are very active chemically. Furthermore, Therminol VP1 is an organic oil that presents low polarity, while carbon nanoparticles are frequently polar. This leads to an added difficulty to obtain a stable nanofluid over time, as the polarity mismatch favours agglomeration and therefore clustering and sedimentation. Different methods to avoid agglomeration of carbon black (CB) nanoparticles in organic solvent have been reported [19]. Surfactant adsorption has drawn a lot of attention among them, given the simplicity and low costs of the process compared to other chemical methods [20]. In this procedure, surfactant molecules are adsorbed in the surface of the nanoparticle, coupling its polarity with that of the base fluid and imposing a steric hindrance to particle accumulation after collisions between them while suspended. According to the mechanisms by which they bond to the nanoparticles, four main types of surfactants exist: anionic, cationic, non-ionic and zwitterionic [7, 20].

Regarding synthetic thermal oils, the most popularly used surfactants are sodium dodecylsulfate (SDS) [13], oleic acid [9, 11, 12], cetyltrimethylammoniumbromide (CTAB) [8, 14, 15], and benzalkonium chloride (BAC) [10, 11, 21]. Although, in most of this studies, nanofluid stability behaviour under high temperature conditions has not been reported. Generally, these surfactants are suitable for their use at temperatures much lower than the nanofluid working temperature [19]. Nanofluid stabilization with surfactants is therefore an important feature to take into account, given that surfactant performance at high temperature working conditions will limit the application of the nanofluid.

In the present work, nanofluids consisting of Therminol VP1 as the base fluid and carbon black nanoparticles have been developed using different surfactants, to make a comparison and analyse their stability at high working temperature conditions. Moreover, other properties, as thermal conductivity and heat capacity of the nanofluid that showed better stability have been studied for different concentrations, and compared to the base fluid.

NANOFLUID SYNTHESIS PROCEDURE

The base fluid used for the nanofluid was an organic synthetic oil made of an eutectic mixture of diphenyl and diphenyl oxide able to perform at high temperature conditions (brand name Therminol VP1, Solutia Inc.). This oil presents high chemical activity under high temperature conditions, therefore a study of the chemical stability of different nanoparticles in Therminol VP1 under high temperature conditions had to be performed initially. Through these tests it could be observed that silica and alumina nanoparticles are affected by Therminol VP1 components, and change their size and morphology. However, carbon-based nanoparticles showed good behaviour in Therminol VP1 even under high temperature conditions. CB nanoparticles (ELFTEX 570, Cabot Corporation) were selected. They consist of spherical amorphous carbon-based particles with a primary particle size of d_p= 10 nm.

Moreover, suitability of three different surfactants was tested: sodium dodecyl sulfate (SDS, Sigma Aldrich Co. Ltd.), sodium dodecylbenzenesulfonate (SDBS, Sigma Aldrich Co. Ltd.), and diphenyl sulfone (DS, Sigma Aldrich Co. Ltd.). SDS and SDBS are ionic surfactants that have been previously used in the literature for different base fluids. However, their stability in Therminol VP1 under high temperature conditions has never been tested. On the other hand, DS is a non-ionic surfactant that shows stability under high temperature conditions and presents high chemical affinity with Therminol VP1 components (both having phenyl functional groups).

Nanofluid elaboration consisted of two steps: firstly, the surfactant was dissolved in the base fluid by magnetic stirring for 1 hour. Then, the carbon black nanoparticles were added and dispersed by sonicating for 3 minutes with an ultrasound probe (Sonopuls HD2200, Bandelin). Surfactant-to-nanoparticle weight ratio was 1:1. Two different concentrations of nanoparticles were studied apart from the base fluid. Thermal oil-based nanofluids with nanoparticle volume concentrations of 3% and 5% (ϕ=0.03 and ϕ=0.05) were prepared.

STABILITY OF THE NANOFLUID

Samples of the different nanofluids were thermally cycled in order to test their stability, since the thermal degradation of surfactants and chemical activity of Therminol VP1 both increase with temperature. Agglomeration and sedimentation over time was tested after high temperature thermal cycles, that were performed in an experimental set-up conformed by a hermetically sealed aluminium cuvette surrounded by a heating ring (see Figure 1). Possibility of pressurizing the cuvette up to 15bar was implemented in the setup to avoid boiling due to the low vapour pressure of Therminol VP1. The system also integrates a pressure transducer and two K-thermocouples, one of them to register and control the cuvette wall temperature and the other to measure the bulk fluid temperature. Bulk fluid temperature and heating and cooling ramps are managed by a proportional–integral–derivative (PID) controller.

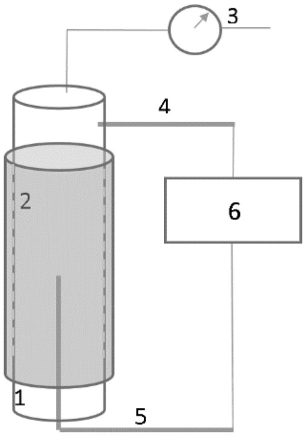

Figure 1 Thermal cycling set-up where (1) is the sealed cuvette, (2) the heating ring, (3) the pressure transducer, (4) the cuvette thermocouple, (5) the fluid thermocouple, and (6) the PID controller.

Ten thermal cycles from 200ºC to 400ºC were performed over each of the nanofluid samples, with heating and cooling rates of 20ºC/min and 10ºC/min, respectively.

The stability characterization tests of the thermally cycled samples were performed attending to the temporal evolution of the amount of light transmitted by the nanofluids. The experimental device (Figure 2) consisting of a quartz cuvette to hold the nanofluid, a 3-mm diameter and 610-nm wavelength laser beam (ThorLabs, MGL-N-532-3W), and a detector system composed of a focusing lens and a photodiode (StellarNet GreenWave, Inc.), which measures the amount of light transmitted by the sample. This simple technique can be easily automated and it provides similar information to that obtained by photo capturing.

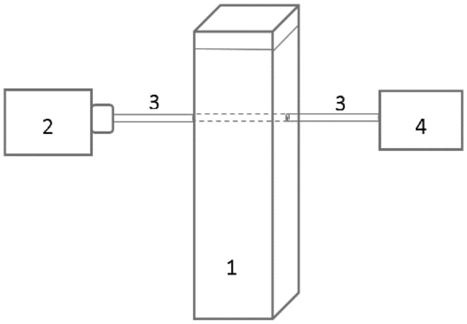

Figure 2 Experimental device for stability measurements, where (1) is the quartz cuvette, (2) the laser diode, (3) the laser beam, and (4) the photodetector.

The transmitted radiation was measured at the upper part of the cuvette for each nanofluid sample, as the changes in concentration produced by sedimentation are more easily observed there. Additionally, half of the laser beam is located outside the sample in order to improve the signal-to-noise ratio. According to this procedure, the nanofluid will be considered stable if the transmitted laser beam intensity does not increase appreciably over time. Stability of the nanofluids was checked over a 5-day period.

SPECIFIC HEAT CAPACITY

The specific heat capacity (Cp) of the samples was measured using a Differential Scanning Calorimeter (DSC, Model DSC2, Mettler Toledo). Sealed high pressure stainless steel crucibles were used in order to ensure self-pressurization of the samples and to minimize evaporation during the experiments. An indium standard was used as a calibration for the DSC and all measurements were performed under a nitrogen gas flow. Following the standard for DSC tests method [22], samples temperature was maintained at 50ºC for 5 minutes, increased up to 350ºC at a rate of 20ºC/min, isothermally maintained for 5 minutes, and finally cooled down to 50ºC at 20ºC/min. This cycle was repeated twice and just the heating ramp was taken into account for the results. Both cycles always presented a difference of less than 10%. DSC measurements of Therminol VP1 showed good agreement with manufacturer data for this the thermal oil (with less than 1% of error), therefore reassuring the reliability of the experimental procedure.

THERMAL CONDUCTIVITY

A KD2 Pro conductimeter (Decagon Devices Inc.) was used to measure thermal conductivity (k) of all the samples. This is a commercial device that measures thermal conductivity through the transient hot wire technique. In this method, a thin metallic wire is embedded in the test liquid, and acts as both the heat source and the temperature sensor. Temperature/time response of the wire to an abrupt electrical pulse is then measured, allowing to obtain the thermal conductivity of the sample from the temperature change of the hot wire in response to the electrical pulse.

For this tests, the samples were put into a sealed glass vial (20 ml), and the sensor was introduced vertically. To carry out the measurements under high temperature conditions, the tube was immersed in a thermostatic bath with a temperature control system. Samples were allowed one hour before any testing for the sample to reach the desired temperature. After that period of time, six measurements were performed for each sample. Within the measurement time, the bath was switched off to avoid possible errors induced by vibrations. It was important to wait for about 15 min between readings to allow the sample to return to the desired test temperature after the heat pulse was applied.

RESULTS AND DISCUSSION

Stability

The stability of four nanofluid samples consisting of Therminol VP1 as the base fluid and carbon nanoparticles along with different stabilizing systems was tested after thermal cycling up to 400ºC:

1)Nanofluid without surfactant
2)Nanofluid stabilized with SDS
3)Nanofluid stabilized with SDBS, and
4)Nanofluid stabilized with SD.

All samples had a volumetric concentration ϕ=0.05 of CB nanoparticles. Figure 3 shows the evolution of the laser radiation transmitted by the four nanofluid samples. An increment in the laser radiation transmitted indicates nanoparticle clustering and sedimentation, as they precipitate causing a concentration gradient on the sample that will allow light to be transmitted more easily in the upper part of the sample.

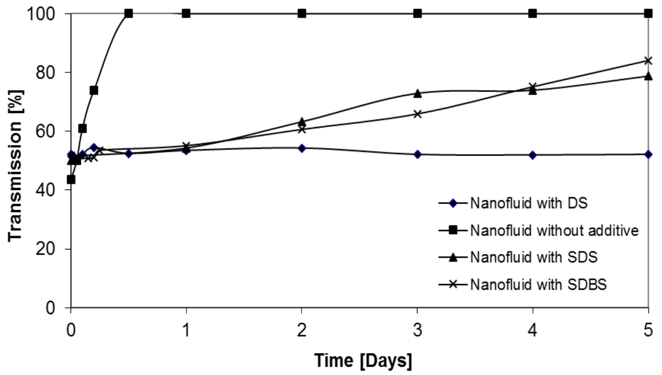

Figure 3 Transmittance dependence of Therminol VP1 nanofluids over 5 days at ϕ=0.05 of CB with different additives used as surfactants.

It can be observed that the nanofluid sample without surfactant (1) presents almost instantaneous sedimentation. Nanofluids with SDS (2) and SDBS (3) show much better stability over time. However, after 1 day measurable sedimentation becomes appreciable. The nanofluid using DS (4) presents the best stability behaviour results, showing no appreciable sedimentation after 5 days. It can be concluded from this tests that DS surfactant does not degrade at high working temperatures and it is still efficient at keeping the stability of the nanofluids under the working conditions. Hence, Therminol VP1 based nanofluid that contains DS as a stabilizer was selected for further thermal properties characterization tests.

Specific heat capacity

In Figure 4, specific heat capacity ratio measurements of Therminol VP1 and Therminol VP1 nanofluids (ϕ=0.03 and ϕ=0.05) can be observed. The subscripts n and bf denote nanofluid and base fluid, respectively.

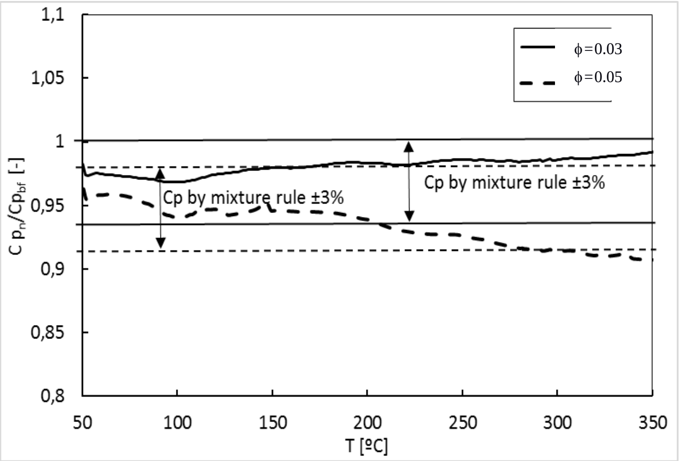

Figure 4 Dependence of specific heat capacity ratio on the temperature at different nanoparticles volume fractions.

As it could be expected, the addition of CB nanoparticles implies a decrease on the specific heat, due to the lower specific heat value of the solid phase with respect to that of the thermal oil. Additionally, changes on the specific heat are observed to have little dependence on temperature. The simple mixture rule can be used to predict the specific heat of suspensions,

$$Cp_{nf} = \frac{\phi(\rho_{np}Cp_{np})+(1-\phi)(\rho_{bf}Cp_{bf})}{\phi(\rho_{np})+(1-\phi)(\rho_{bf})} \qquad (1)$$

where ϕ denotes solid volume fraction, ρ density, and np and bf subscripts correspond to nanoparticle and based fluid, respectively.

The experimental data in Figure 4 corresponds well with the predictions provided by the mixture rule (see equation 1), as reported for lower temperatures in previously published studies [8].

Thermal conductivity

Figure 5 shows the thermal conductivity ratios of Therminol VP1 base fluid alone and Therminol VP1 based nanofluids (with ϕ=0.03 and ϕ=0.05 CB volume fractions).

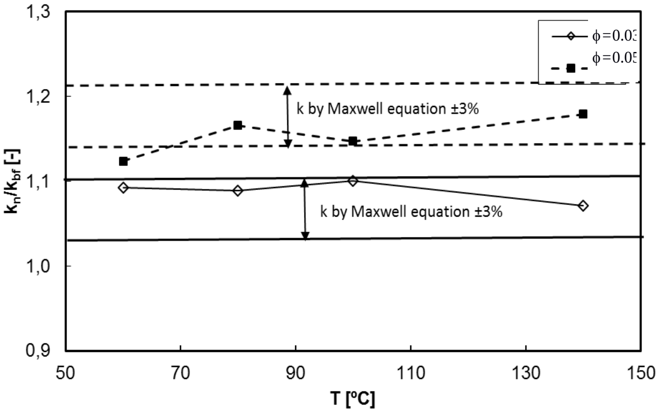

Figure 5 Conductivity ratio dependence on the temperature at different nanoparticle volume fractions.

As it can be observed, both nanofluids present higher values of thermal conductivity than that of the base fluid, with average increments of 9% and 15% for ϕ=0.03 and ϕ=0.05 nanoparticle volume fractions, respectively. In addition, it can be seen that the increase in the thermal conductivity does not depend on the test temperature and that it is consistent with the increments provided by the Maxwell equation (see equation 2), as reported in previously published studies that were conducted at lower temperatures [8, 10-11].

$$k_m = \left[\frac{k_p+2k_f+2(k_p-k_f)v_f}{k_p+2k_f-(k_p-k_f)v_f}\right]k_f \qquad (2)$$

CONCLUSIONS

In this work a new formulation of a heat transfer fluid based on Therminol VP1 and carbon nanoparticles has been proposed using diphenyl sulfone as a stabilizer. This surfactant was the only one that provided good stability of the samples even under high temperature conditions (up to 400ºC). Other surfactants frequently used in the literature were found to fail due to thermal degradation and loss of efficiency at high temperatures.

The new formulation was characterized in terms of thermal properties under high temperature conditions for two different nanoparticle concentrations. Thermal conductivity increases with solid content following the Maxwell equation, as expected, meaning an improvement of this feature in the nanofluid with respect to the base fluid. The specific heat decreased for the nanofluids according to the mixture rule.

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