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# Stabilization and characterization of a nanofluid based on a eutectic mixture of diphenyl and diphenyl oxide and carbon nanoparticles under high temperature conditions

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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 400 °C. 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. 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 400 °C showed the higher performance of this additive compared to others commonly used in the literature. Thermal conductivity, heat capacity, and viscosity of the nanofluids at 3 vol% and 5 vol% were characterized from 50 °C to 350 °C. Finally, the Mouromsteff number was calculated to determine the heat transfer enhancement provided by the use of nanofluids.



## 1. Introduction

Thermal oils are widely used as heat transfer fluids (HTFs) for medium and high temperature applications in several industrial processes such as oil and gas processing, the manufacture of pharmaceuticals, the production of chemicals, and in Concentrated Solar Power (CSP) plants. There are different types of thermal oils, depending on their composition. Synthetic thermal oils are widely used due to their low viscosity and high stability under high temperature conditions with operating temperatures between −80 °C and 365 °C/400 °C. Among them, the synthetic thermal oil composed of a eutectic mixture of 73.5% diphenyl oxide and 26.5% diphenyl (brand name Therminol VP1) presents high stability with continuous bulk operation temperatures of 400 °C. This type of thermal oil is widely used in CSP plants, since the efficiency of the plant depends to a great extent on the maximum temperature of the HTF. However, thermal oils present low thermal conductivity, thus limiting the heat transfer performance of this type of HTF.

Nanofluids are defined as engineered colloidal suspensions of nanoparticles, and they have potential applications in heat transfer processes, among others. They were first proposed by Masuda [1] and Choi [2] in the early 90s. Nanofluids are composed of a liquid HTF, nanoparticles, and stabilizers (if needed). In this way, nanofluids allow a solid to be included within a liquid, transferring, to some extent, the solid properties to the liquid and keeping, also to some extent, the liquid transport properties. Over the last 20 years nanofluids have been extensively investigated as advanced HTF with enhanced thermal properties by the addition of nanoparticles [3–6]. One of the key benefits of nanofluids is the increased thermal conductivity of the base fluid. As their main drawback, nanofluids present higher dynamic viscosity values and possible stability problems.

Nanofluid stability is critical to its practical application and different techniques as Z potential, Dynamic Light Scattering (DLS), Scanning Electron Microscopy (SEM), Transmission Electron

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**Nomenclature**

| | |
|---|---|
| CSP | Concentrated Solar Power |
| CB | carbon black |
| DSC | Differential Scanning Calorimetry |
| DLS | Dynamic Light Scattering |
| DS | diphenyl sulfone |
| HTF | heat transfer fluids |
| NF | nanofluids |
| NP | nanoparticles |
| PT | Parabolic Trough |
| SEM | Scanning Electron Microscopy |
| TEM | Transmission Electron Microscopy |
| TES | Thermal Energy Storage |
| TGA | Thermogravimetric Analysis |

*Symbols*

| | |
|---|---|
| Cp | specific heat capacity of nanofluid |
| k | thermal conductivity |
| μ | viscosity |

*Subscripts*

| | |
|---|---|
| bf | base fluid |
| n | nanofluid |
| np | nanoparticle |

Microscopy (TEM), UV–Visible spectrometry or photo capturing can be used to determine it with different limitations [7–13].

Most of the work related with synthetic thermal oils-based nanofluids published to date uses aromatic-based oils [8,14–18]. However, studies that have been published using Therminol VP1 as the base fluid are scarce [19–21]. Besides, carbon nanoparticles have been employed in many previous studies to enhance the base fluid properties [22–24]. Carbon nanoparticles present high chemical stability with most chemical compounds and this makes them suitable for use with Therminol VP1, which is composed of two chemically very active compounds. Therminol VP1 is organic and has low polarity, whereas carbon nanoparticles are generally polar. This polarity mismatch makes it especially difficult to obtain a nanofluid that is stable over time. There are different approaches to avoid carbon black (CB) nanoparticle agglomeration in organic solvents, such as partial oxidation, covalent bonding, non-covalent bonding, and encapsulation [25]. Among them, surfactant adsorption has aroused a great deal of interest, since the process is simple and low-cost compared to other chemical routes [26].

Popular surfactants that have been used in synthetic thermal oil nanofluids are sodium dodecylsulfate (SDS) [19], oleic acid [14,16–18], cetyltrimethylammoniumbromide (CTAB) [8,20,21], and benzalkonium chloride (BAC) [9,15,16]. However, in most of these studies, nanofluid stability has not been characterized under high temperature conditions. Moreover, the thermal stability of these surfactants in other systems has been shown to be much lower than the working temperature of the nanofluid [25]. Hence, nanofluid stabilization using surfactants presents important challenges, due to its high temperature working conditions, which limit the surfactant options available.

The present work evaluates, at high temperature conditions, the stability, thermal and rheological properties of a thermal oil widely used in several industrial processes modified with nanoparticles. Therefore, a nanofluid based on Therminol VP1 using carbon black nanoparticles and different surfactants has been developed, and its stability under high temperature conditions has been tested. In addition, the thermal conductivity, heat capacity, and viscosity of the most stable nanofluid have been characterized with different nanoparticle concentrations under high temperature conditions. Finally, the heat transfer enhancement of the nanofluids has been calculated using the Mouromsteff number.

## 2. Methods

### 2.1. Nanofluid synthesis procedure

The base fluid used was an organic synthetic oil made of a eutectic mixture of diphenyl and diphenyl oxide suitable for high working temperature conditions (brand name Therminol VP1, Solutia Inc.). Therminol VP1 presents high chemical activity under high temperature conditions. Consequently, a preliminary study of the chemical stability of different nanoparticles in Therminol VP1 under high temperature conditions was performed. These tests showed that nanoparticles such as silica or alumina are affected by the Therminol VP1 components, changing their size and morphology, and only carbon-based nanoparticles are able to work in Therminol VP1 under high temperature conditions. CB nanoparticles (ELFTEX 570, Cabot Corporation) were selected, since they are carbon-based and inexpensive. They consist of spherical amorphous carbon with a primary particle size of dp = 10 nm.

In addition, three different surfactants were used: 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 used in the literature for different base fluids, although their stability under high temperature conditions using Therminol VP1 has not been tested. DS is a non-ionic surfactant that was selected because it is stable under high temperature conditions and presents high chemical affinity with Therminol VP1 components (both have phenyl functional groups).

The nanofluid synthesis procedure was performed in two steps: the surfactant was first dissolved in the base fluid by magnetic stirring for 1 h. Then the carbon black nanoparticles were added and dispersed using an ultrasound probe (Sonopuls HD2200, Bandelin) for 3 min. The surfactant-to-nanoparticle weight ratio was 1:1. Two different nanoparticle concentration were synthetized, so that the influence of this variable on the experimental results could be evaluated. The nanoparticle concentrations were selected so that the effect on the thermal and rheological properties could be noticed and that the stability of the nanofluid could be assured. Finally, thermal oil-based nanofluids with nanoparticle volume concentrations of 3% and 5% ($\phi = 0.03$ and $\phi = 0.05$) were prepared.

### 2.2. Stability of the nanofluid

The stability of the nanofluid was tested using thermally cycled samples, since the chemical activity of Therminol VP1 and thermal degradation of surfactants both increase with temperature. Thermal cycling was performed in a set-up consisting of a hermetically sealed aluminum cuvette heated by a heating ring (see Fig. 1). Due to the low vapor pressure of Therminol VP1, the cuvette can be pressurized up to 15 bar to avoid boiling. The system integrates a pressure transducer and two K-thermocouples, one of them to control the cuvette wall temperature and the other to measure the bulk fluid temperature. The bulk temperature of the fluid and heating and cooling ramps are controlled by a proportional–integral–derivative (PID) controller.