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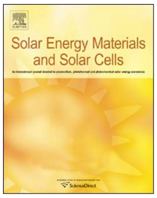

Rheology of Solar-Salt based nanofluids for concentrated solar power. Influence of the salt purity, nanoparticle concentration, temperature and rheometer geometry

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ABSTRACT

Solar Salt-based nanofluids have attracted significant scientific interest in recent years due to their improved thermal properties, making them strong candidates as thermal energy storage materials and/or heat transfer fluids in CSP plants. There have been reports on increased specific heat due to the addition of nanoparticles, however, there is a lack of comprehensive information on other essential properties affecting the heat transfer, such as the viscosity. This article concerns the rheological behaviour of nanofluids made of Solar Salt (mass percentage at 60% $NaNO_3$ – 40% KNO_3) as the base fluid and silica or alumina nanoparticles as additives. The evolution of these nanofluids viscosity as a function of the shear rate (1–1000 s^{-1}) at a temperature range of 250–400 °C was measured and analysed. The impact of the salt purity (refined or industrial grade), the nanoparticle concentration (0.5–1.5 wt%) and the rheometer measuring configuration (coaxial cylinder or parallel plate) are examined. The results showed in general a Newtonian behaviour of the nanofluids with independency of the rheometer configuration. The relationship between the viscosity and the temperature follows an Arrhenius model. The influence of the nanoparticle concentration on the viscosity of the refined grade Solar Salt is analysed according to the Maron-Pierce and Kriegher-Dougherty models for the nanofluids containing alumina and silica nanoparticles respectively, due to their different shape.

1. Introduction

The worldwide increasing energy demand compels to use and develop new technologies based on renewable resources. The main disadvantage of these sustainable energy sources is their intermittence and thus, their low availability on demand in comparison to the non-renewable energy resources. In this context, the Concentrated Solar Power (CSP) technology is of high importance due to its proven dispatchability and efficiency [1–5]. Although the electricity costs are still high, they are expected to decrease consistently in the years to come [6]. The use of a Thermal Energy Storage (TES) system in the current CSP plants allows to size the storage system according to the requested plant operation time. For example, at the moment Termosol 1 and 2 (solar trough technology) in Spain reach 9 h of thermal storage [7] and Gemasolar (solar central receiver system) even reachs 15 h, allowing in some periods the daily continuity production [8,9]. The presently employed TES systems store the energy as sensible heat. They consist of two tanks filled with a molten salt at different temperatures: the "cold" tank is around 300 °C and the "hot" tank at 400 °C in the solar plants with parabolic through technology, and 565 °C in the plants with power tower technology, respectively. This salt is a mixture of sodium and potassium nitrate (60:40 wt) known as Solar Salt, with a melting point

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of 238 °C [10,11]. This mixture is used instead the eutectic one ($NaNO_3$:KNO_3 50:50 wt) to reduce the material costs [12]. Presently, the working temperature in the solar field is becoming increasingly higher in modern central receiver plants (tower), and therefore, Heat Transfer Fluids (HTFs) with a broader range of thermal stability are required. So far, thermal oils (Dowtherm™, Therminol® VP-1) have been mostly used as HTFs in parabolic trough plants. However, their degradation temperature is very low (400 °C). However, they have many drawbacks such as their toxic nature, high cost, low degradation temperature (400 °C) and the need of working under pressure to avoid their degradation. Hence, Solar Salt represents a great alternative to these oils with a wider range of working temperatures (250–600 °C), low cost and harmless for the environment.

Despite these advantages, its thermal properties (specific heat and thermal conductivity) are poor and there is still a large potential to improve them and/or to decrease their minimum working temperature, limiting the nocturnal losses and making the Operation & Management tasks easier [13–16]. A simple and cost-effective way to enhance their thermal conductivity and specific heat consists of adding nanoparticles to the Solar Salt. This new type of materials is known as Molten Salt-Based Nanofluids (MSBNFs) and has attracted great interest on the scientific community in recent years [17,18]. The main feature of these nanofluids is the relevant specific heat increment in comparison with the base salt, which has been systematically observed [19–23]. The amount of stored heat is directly related to the specific heat and as a result, the enhancement of this property allows storing more energy per unit volume, thus extending the duration of CSP plant production. Incidentally, only MSBNFs show the enhancement of the specific heat, while nanofluids based on water or oils as the base fluid do not show it [24]. The mechanisms which govern the interaction between the nanoparticles and the molten salt are not still well-known, although some hypotheses have been proposed in the literature [25,26]. Due to the encountered evidences, most of the scientific research on this field, including the analysis of new molten salts mixtures, has been devoted to the study of the specific heat and only some few works deal with the thermal conductivity [27–30], while other properties have received very little attention.

Apart from the MSBNFs thermal properties, their rheological performance is of high importance for their industrial implementation as HTFs or in the TES system [23,31–34]. The introduction of the nanoparticles into the molten salt leads to the rise of the viscosity. This will increase the pumping energy required and could occasionally require design changes of some elements. A commitment should be reached between the larger heat transfer rates achieved by the MSBNFs and the higher costs associated to the pumping [31]. In addition, heat transfer is directly affected by viscosity because the Reynolds number changes. In spite of the industrial relevance of the rheological properties of the MSBNFs, the research on these properties is still very scarce [23,31–34].

1.1. Factors influencing the viscosity

The viscosity of the MSBNFs depends on many factors, such as the shear rate, the temperature and the nanoparticle concentration. Besides, the geometry of the rheometer is also a factor to be considered in non-Newtonian fluids, which is typical of colloidal systems [35,36]. Even though the dependence of the viscosity on the shear rate and the temperature is of general knowledge, a brief review has been included in Appendix A to help in the understanding of this article. The influence of the nanoparticle concentration is detailed hereafter, as a significant property owned by the nanofluids.

Several models are proposed in the literature to estimate the fluid increment of viscosity due to the presence of solid particles (a two-phase mixture) [37,38]. These models take into account the particle concentration and their shape, as well as their agglomeration caused by the flowing fluid. They have been developed from the pioneering model by Einstein (Eq. (1)), which considers the existence of non-interacting hard spheres on a fluid with a volume fraction smaller than 1%.

$$\mu_R = 1 + 2.5\cdot\varphi \tag{1}$$

where μ_R is the relative viscosity (viscosity of the dispersion/viscosity of the base fluid) and φ is the volume concentration of particles.

On the limited literature about the rheology of MSBNFs, the Krieger and Dougherty (K-D) model [31,32,34] and the Maron – Pierce (M-P) model [39] have been used to explain the viscosity increments of the nanofluids. The K-D model (Eq. (2)) is suitable for nanofluids which contain spherical nanoparticles. It takes into account their agglomeration to estimate the viscosity.

$$\mu_R = \left(1 - \frac{\varphi_a}{\varphi_m}\right)^{-[\mu]\cdot\varphi_m} \tag{2}$$

where μ_R is the relative viscosity, φ_a is the volume fraction of aggregates, φ_m is the maximum volume fraction at which flow can occur and μ is the intrinsic viscosity. Considering $\varphi_m = 0.605$, $[\mu] = 2.5$ and $\varphi_a = \phi\,(a_a/a)^{3-D}$ with $D = 1.8$, the K-D modified model is obtained (Eq. (3)) [31,32,34].

$$\mu_R = \left(1 - \frac{\phi}{0.605}\left(\frac{a_a}{a}\right)^{1.2}\right)^{-1.5125} \tag{3}$$

where μ_R is the relative viscosity, ϕ is the volume concentration of nanoparticles, a_a is the size of aggregates and a is the size of the primary nanoparticles.

The M-P model (Eq. (4)) is suitable to predict the viscosity of nanofluids with fibre-shaped nanoparticles [39].

$$\mu_R = \left(1 - \frac{\varphi_a}{\varphi_m}\right)^{-2} \tag{4}$$

where μ_R is the relative viscosity, φ_a is the volume fraction of aggregates, φ_m is the maximum volume fraction at which flow can occur. This parameter can be evaluated according to the aspect ratio of the nanoparticles, r, as explained in [39] (Eq. (5)).

$$\varphi_m = \frac{2}{0.321r + 3.02} \tag{5}$$

1.2. Rheology of Solar Salt and MSBNFs

The viscosity of MSBNFs made of molten carbonates with multi-Wall Carbon Nanotubes (MWCNTs) accounting for 1, 2 or 5 wt% was studied by Jo and Banerjee [32]. Jung et al. [31,34] and Lasfargues et al. [23,33] studied the viscosity of the molten Solar Salt with silica nanoparticles (0.5 and 1 wt%) and molten Solar Salt with copper oxide nanoparticles (0.1 wt%). The viscosity increase due to the presence of the nanoparticles is described in all these works: 11%, 93% and 1130% for the MWCNTs mass concentrations of 1%, 2%, and 5%, respectively [32]. Jung [31] found a viscosity increment between 39% and 65% when silica nanoparticles were added to obtain a concentration of 0.5% and an increment between 57% and 68% when 1% concentration was produced. The viscosity increment reported by Lasfargues et al. [33] at the temperature range from 250 °C to 450 °C was comprised between 4.7% and 18.3%. Finally, Jo et al. [34] determined a viscosity increment of 63% at 300 °C and 79% at 400 °C. The reviewed literature, indicates that there is not an agreement on the Newtonian [23,33] or non-Newtonian behaviour [31,32,34] of the nanofluids though the well-known Newtonian nature of the molten salts [23,31,33,34]. The nanoparticle agglomeration during the tests may influence the results, as well as the measuring method employed.

The viscosity of the Solar Salt has been measured by several authors in different conditions, as gathered in Table 1. Most of them analyses the equimolar mixture of sodium and potassium nitrate (45.7:54.3 wt%) instead of the industrial Solar Salt composition (60:40 wt%)