Investigation of a single wall carbon nanohorn-based nanofluid in a full-scale direct absorption parabolic trough solar collector

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Abstract

An experimental investigation on the use of nanofluids as working fluids and direct absorbers in a full-scale concentrating collector is presented. The nanofluid consists of a suspension of single wall carbon nanohorns in distilled water with a concentration of 0.02 g L$^{-1}$. The thermo-physical properties are the same as those of the base fluid, but the presence of carbon nanoparticles greatly enhances the optical characteristics. A direct absorption receiver has been designed and set up to investigate the capability of the nanofluid to absorb the concentrated sunlight. The receiver exhibits a flat geometry and has been designed for installation on an asymmetric parabolic trough, where the concentrated solar flux locally reaches 100 kW m$^{-2}$ under clear-sky conditions. Results show that the application of a carbon nanohorn-based nanofluid in a concentrating collector displays an efficiency comparable to that obtained with a surface receiver tested in the same system. However, such performance is not maintained for a long time because of lack of stability of the absorbing fluid.

Keywords: Direct absorption solar collector; parabolic trough; single wall carbon nanohorn.
1. Introduction

The large use of photovoltaic, concentrated solar power and solar thermal technologies is expected to play a crucial role in the future provided that the conversion of solar energy become more efficient and cost-effective. In particular, significant technological development can be achieved also for solar thermal collectors in heating and cooling applications of industrial, commercial, residential and service sectors. In conventional solar thermal collectors, the solar irradiance heats up an absorber surface provided by a selective coating, hence the major part of the heat is transferred to the working fluid, driven by a temperature difference. In typical configurations, conductive and convective thermal resistances between the absorber and the fluid makes the effectiveness of solar-to-thermal energy conversion quite limited because of high heat losses from the surface absorber to the surroundings. Innovative absorber elements providing enhanced heat transfer, such as roll-bond [1] and bar-and-plate absorbers [2], have been proposed by the present authors among others.

Recent advances in nanotechnologies have led to the production of nanofluids, which consist of dispersions of nanoparticles in a base fluid to improve the fluid functional properties [3]. At first, they have been proposed as working fluids in surface-absorption solar thermal collectors, since they were supposed to possess superior thermal properties as compared to the conventional working fluids. Actually, ambiguous results have been obtained when assessing the enhancement of thermal convection by adding nanoparticles in a fluid [4, 5]. On the other hand, numerous studies have demonstrated that the optical properties of the base fluid can be dramatically enhanced even with very low amounts of specific nanoparticles [6, 7]. In direct absorption solar collectors (DASCs), conceived by Minardi and Chuang [8], the incoming solar irradiance is directly and volumetrically absorbed by the nanoparticles and transferred to the surrounding fluid as thermal energy with very high heat transfer coefficients. As compared to the conventional surface-absorption solar collectors, the total thermal resistance is lower, the fluid bulk represents the hottest element, the optical efficiency increases and the convection heat losses diminish because of the lower surface temperature. DASCs may therefore lead to higher thermal efficiency and lower cost due to the absence of a selective surface. The working fluids employed in the past, such as Indian ink and microparticle-based fluids were unsafe, toxic and unstable, causing fouling of hydraulic loops, clogging of pumps and erosion issues. The application of nanofluids in DASCs may overcome these drawbacks, since the presence of a small amount of nanoparticles should facilitate the preparation of stable fluids, entails a negligible change in viscosity and minimizes mechanical erosion and chemical corrosion [9]. Furthermore, nearly total absorption of the solar spectrum energy can be achieved by properly tuning the kind and concentration of nanoparticles in the base fluid.

1.1 Previous experimental studies on DASCs using nanofluids

Experimental works available in the literature mainly deal with tests on laboratory-scale solar collectors which provide critical insights into the photo-thermal conversion mechanisms and useful indications for the design of larger DASCs. Tests under solar simulators at low and medium solar concentrations and no-flow conditions have been performed at low temperature (below 100°C) [10-
16]. They involved the measurement of temperature distribution in the fluid bulk over time and stagnation temperature or peak temperature achieved. These works allowed assessing the optimum nanoparticle concentrations or size, leading to higher stagnation or peak temperature in a given nanofluid and comparing the absorption properties of different nanofluids. Similar tests have been carried out in no-flow devices with larger dimensions such as transparent glass cells [17] or glass-in-glass evacuated tubes [18]. Jin et al. [19] reported that the efficiency obtained using gold nanoparticles in water inside a glass-in-glass evacuated tube under natural sunlight decreased with increasing solar irradiance. An experimental study under stagnation was performed by Xu et al. [20] using water with magnetic iron nanoparticles as the working medium in a glass-in-glass evacuated tubes. Some authors presented the trend over time of the specific absorption rate, which compares the absorption capability of the nanofluid to that of the pure base under no-flow conditions. Actually, initial values of specific absorption rate may represent a qualitative parameter to preliminary assess the application of a nanofluid in a DASC.

In experimental investigations with nanofluids flowing across lab-scale devices, the mass flow rate is low enough so that the thermal efficiency can be defined from measurable temperature rises. Otanicar et al. [21] performed tests with aqueous nanofluids containing graphite nanoparticles, silver nanoparticles and carbon nanotubes at low temperature (up to 45°C) on a direct absorption micro-collector under 1000 W m\(^{-2}\) irradiance. Lee et al. [22] compared the performance of a surface absorption and a direct absorption lab device under concentrated irradiance (22 suns). A suspension of multi-wall carbon nanotubes in water has been considered for these tests. Taylor et al. [23] tested a direct absorption mini-receiver of a parabolic dish concentrating collector having a geometric concentration ratio of around 400 suns and working with graphite nanoparticles in Therminol oil at temperatures up to 250°C. The results univocally showed that it exists an optimum nanoparticle concentration beyond which the efficiency levels off or even decreases.

There are few studies concerning the application of nanofluids in small prototypes of full-scale DASCs. To the best of the authors' knowledge, available investigations on nanofluid-based non-concentrating direct absorption technologies regard only flat plate solar collectors. Gupta et al. [24] investigated the performance of a full-scale DASC under natural sunlight with an alumina-based aqueous nanofluid. Karami and coworkers [25, 26] tested a DASC for domestic water heating with either CuO nanoparticles or multi-wall carbon nanotubes in water and ethylene glycol mixture. Using both nanofluids, the collector thermal efficiency increased with volume fraction and flow rate but with an asymptotic trend. The same prototype of volumetric flat plate collector and the same test procedure were considered by Vakili et al. [27] to investigate the application of three nanofluids with nanoplatelets weight fractions of 0.0005, 0.001 and 0.005, finding that the efficiency increased.

With respect to the use of nanofluids as working fluids and direct absorbers in concentrating solar collectors, the studies described in the literature concern applications in small prototypes involving low concentrated solar fluxes (lower than 12 kW m\(^{-2}\)). Muraleedharan et al. [28] examined the performance of Al\(_2\)O\(_3\) dispersions in Therminol with concentrations from 0.025 to 0.1 %vol and a constant flow rate of 0.5 L s\(^{-1}\). The single-axis tracking collector comprised four linear Fresnel lenses (0.55 m x 0.18 m) focusing the direct solar irradiance on four evacuated glass-in-glass tube receivers.
with external and internal diameter of 15 mm and 10 mm, respectively. It was arranged in a test rig equipped with a storage tank, where the collector outlet temperature and the net stored energy were measured as a function of time. Results showed that using the highest nanoparticles concentration, the 28 liters tank temperature increased from 25°C to 130°C within 3.5 hours. Li et al. [29] compared the performance of a surface (black-chrome coated copper tube) and a volumetric solar absorber (glass tube) arranged in a low profile solar concentrating collector consisting of a linear Fresnel lens, a glass envelope, a compound parabolic concentrator and an absorber element with a geometrical concentration ratio of about 5 and with an internal tracking system. Suspensions of multi-wall carbon nanotubes in water and Therminol with concentration of 50 mg L\(^{-1}\) were chosen as working fluids. Tests were carried out under standardized steady-state outdoor conditions at a mass flow rate of 0.02 kg s\(^{-1}\) and at inlet temperatures up to 250°C. Results highlighted that the performance of the surface absorber was higher than that of the volumetric receiver. The authors pointed out that there is much room for reducing the heat losses in the direct absorption solar absorber while maintaining its cost-effectiveness as compared to a conventional surface absorber. Menbari et al. [30] presented the application of a CuO-water nanofluid in a direct absorption parabolic trough solar collector. The single-axis tracking parabolic concentrator had a reflectivity of 65%, an aperture width of 0.8 m and a length of 1 m. The evacuated tubular receiver consisted of two concentric glass tubes having a diameter of 36 mm and 20 mm, respectively. The estimated peak of concentrated solar flux was around 12 kW m\(^{-2}\). The results indicated that the thermal efficiency of the concentrating collector increased with mass flow rate and nanoparticle volume concentration. Similar trends were obtained by the same authors when studying the use of different binary nanofluids in the mentioned parabolic trough collector [31].

1.2 Present study

The study of the available open literature reveals that, to date, the experimental investigation of nanofluids in full-scale DASCs is in its infancy and a large effort is required to promote the development of this technology and solve existing issues. The present paper is a new contribution in this research line. It reports on the investigation of single wall carbon nanohorn(SWCNH)-based aqueous nanofluid in a direct absorption receiver of a full-scale parabolic trough solar collector operating in the medium temperature range. A new volumetric planar receiver has been designed in order evaluate the optical capability of the considered nanofluid to absorb a high concentrated solar flux. The original points of this work are twofold: at first, test runs have been performed under realistic operating conditions at intense concentrated solar flux (up to 100 kW m\(^{-2}\) on the focal line of the concentrator); secondly, the experiments have been carried out using a nanofluid with excellent optical properties [32] and potentially low cost, but never characterized in full-scale collectors to date.

2. Nanofluid preparation and optical characterization

The concentration of nanoparticles in the base fluid has been observed to have a significant impact on the optical behavior of the nanofluid. In fact, at low particle mass fractions, part of the incident irradiance is not absorbed by the nanofluid. On the other hand, at high particle concentrations,
nanofluid may become unstable, while absorption occurs at the top layer of the nanofluid, resembling thus the thermal behavior of a conventional surface absorber. Therefore, it is fundamental to characterize the optical properties of the chosen nanofluid at its specific concentration in order to meet the optical characteristics of the considered volumetric absorber. Furthermore, the stability of nanofluids is fundamental for the maintenance of thermal, rheological and optical properties during their application in DASCs. When dispersed in a liquid, nanoparticles tend to aggregate and precipitate, leading to a variation in the fluid composition and, consequently, in its properties. Hence, the optimization of the nanofluid preparation method is essential [33].

2.1 Nanofluid preparation

Carbon nanohorns are tiny graphene sheets, wrapped to form horn-shaped cones with a half-fullerene cap, having 30-50 nm length and 2-5 nm diameter. They generally group together and form aggregates (spherical clusters or bundles) similar to "dahlia" flowers or buds. These nanostructures were provided by the company Carbonium S.r.l. and were produced by a process based on rapid condensation of carbon atoms without any catalyst and with highly reduced production costs [3934] and an estimated market price lower than 3 €/g. The morphological characterization of the nanoparticles was performed by Field Emission - Scanning Electron Microscopy (FE-SEM) with a SIGMA Zeiss instrument (Carl Zeiss SMT Ltd, UK). Figure 1 reports an example of FE-SEM micrograph for SWCNHs powder. The mean dimension of carbon nanohorns, evaluated by means of the software ImageJ IJ 1.46r, was equal to 80 ± 6 nm. The aggregation is due to the drying process in preparing the specimen to perform FE-SEM observation.

Figure 1. FE-SEM micrograph of carbon nanohorn powder.

The SWCNHs suspension for tests in a full-scale concentrating collector was prepared at the Institute of Condensed Matter Chemistry and Technology for Energy (ICMATE) of the National Council of the Research (CNR) in Padova, Italy. The nanofluid preparation described here is schematically summarized in Figure 2.
The suspension containing 0.02 g L\(^{-1}\) of SWCNHs in a water solution where sodium dodecyl sulfate (SDS) was chosen as a surfactant (SWCNH:SDS = 4:1 by weight) was prepared according to the following procedure. First, 250 ml of a solution containing 0.005 g L\(^{-1}\) of SDS in water was prepared, afterward, 0.05 g L\(^{-1}\) of SWCNHs were dispersed in this solution by a first homogenization with an ultrasonic processor (VCX 130, Sonics & Materials) at 20 kHz and 65 W for 10 min. Therefore, a high-pressure homogenizer (Panda, GEA Niro Soavi, 1000 bar) was employed for 15 min to optimize the dispersion. Finally, all batches prepared were diluted to achieve 7 liters of the 0.02 g l\(^{-1}\) of SWCNHs suspension.

The use of SDS as surfactant results fundamental to achieve a stable nanofluid under laboratory conditions. In fact, the \(\zeta\)-potential for suspensions with SDS as surfactant resulted much higher in modulus (-44 mV) than that for suspensions without SDS (about -8 mV). Furthermore, the homogenization process was optimized: samples of nanofluids have been produced considering various homogenization times (from 0 to 60 min homogenization) and, for each sample, a quantitative analysis on SWCNHs size distribution in water was carried out by Dynamic Light Scattering (DLS, Zetasizer Nano, Malvern). This analysis reveals the possible presence of unwanted settling and clustering phenomena. The measurements were performed for 15 days on a static sample (i.e. not undergone to stirring before measurements) and a 15 min homogenization processing has been found to be the optimum in terms of stability. Figure 3 reports the mean aggregate size measured by means of the DLS technique for 15 days in suspensions for non-homogenized (0 min) and for 15 min homogenized sample: the decreasing of aggregate size and the stability with time of the sample after 15 min homogenization is clearly depicted in Figure 3.

Figure 2. Schematic of the nanofluid preparation.
The suspension stability with temperature was qualitatively evaluated by placing samples in an autoclave at 150°C and about 5 bar for 24 hours. Only the samples prepared with homogenization showed no aggregation and/or settling after this test. Figure 4 shows a SEM micrograph of the homogenized sample, where no modifications of carbon nanohorns morphology were detected as compared to the only sonicated sample.

The compatibility and stability of the SWCNHs suspension with the materials used in the test rig have been verified in laboratory tests conducted by immersion of sample of the material in the prepared suspension. No aggregation and/or settling has been observed.

Considering the very low SWCNHs concentration, the thermo-physical properties (thermal conductivity and viscosity) were verified to be analogous to the base fluid (water).

Figure 3. Mean aggregate size measured by DLS for 15 days in suspensions for non-homogenized (0 min) and for 15 min homogenized sample.

Figure 4. SEM micrograph of 15 min homogenized sample.
2.2 Optical characterization

According to a preliminary optical characterization [35] of SWCNHs nanofluid under laboratory test conditions, the suspension containing 0.02 g L\(^{-1}\) of SWCNHs in water assures the complete extinction of the incident light in a depth greater than about 24 mm (Figure 5). From the same Figure 5, it can be appreciated how SWCNHs dramatically change optical properties of the fluid, as pure water has a considerable lower sunlight absorption.

![Figure 5. Comparison of the absorbing energy capabilities of a suspension containing 0.02 g L\(^{-1}\) of SWCNHs in water (continue line) and pure water (dashed line) [35].](image)

For diagnostic purposes, considering the different preparation technique of the present suspension with the one presented in [35], the optical extinction spectra have been measured in the spectral range 200-2500 nm on the sample studied in this experiment, by the Italian National Institute of Optics (INO) of the National Council of the Research (CNR) in Florence, Italy. The measurement is carried out using a double-beam spectrophotometer (Perkin Elmer Lambda 900) and holding the sample in cells with 50 ±1140 µm-thicknesses [36]. Figure 6 reports the spectral extinction coefficient of the suspension tested in the concentrator (0.02 g L\(^{-1}\) of SWCNHs in water) in the spectral range 200-1400 nm. A good agreement with previous works was found.

It should be noticed that for carbon nanohorn suspensions, the extinction gives a good approximation of absorption properties since the optical scattering can be considered negligible [37, 38].
3. Experimental apparatus

The direct absorption concentrating solar collector considered in this work is composed by a prototype of an asymmetrical small parabolic trough [2] which concentrates the incoming direct normal solar radiation on an ad-hoc designed volumetric planar receiver. The collector has been installed in the Solar Energy Conversion Lab of the Industrial Engineering Department, at the University of Padua, Italy.

3.1 Solar concentrator

The cross section of the considered linear concentrator is a half of a parabola that extends from the vertex to the mirror rim with an angle of 78.7° (Figure 7). The aperture width is 2.91 m and the length of the trough is equal to 2.4 m, resulting in an aperture area of 6.984 m². The focal length of the parabola is 1.81 m. Four back silvered glass facets form the reflecting surface. The manufacturer (Ronda High Tech S.r.l.) provides a nominal solar reflectivity of 96%. This reflective surface is cut at 35 mm from the vertex line on the parabolic profile, allowing the placement of the receiver with no shading on the optics itself. A two-axes solar tracking system points the concentrator to the sun in order to have the direct irradiance normal to the aperture area avoiding any cosine loss while working. The motion of the tracking system is regulated by a solar algorithm when approaching the sun and by a light sensor when achieving the best receiver alignment. The solar tracking error is less than 0.2°.
The particular geometry and tracking system of the present concentrator have been adopted for experimental research purposes to facilitate the access to the focal line, the arrangement of sensors and the device control. Furthermore, the peculiar asymmetric geometry of this parabolic trough concentrator is suitable to be coupled with a receiver displaying a flat geometry absorber rather than a tubular receiver.

This concentrator is part of the test circuit whose schematic is shown in Figure 8. This test rig includes the new volumetric receiver.
3.2 Volumetric receiver

A new volumetric planar receiver has been designed and fabricated to test the direct absorption of the concentrated solar radiation in a volume of fluid. Sketches of the proposed receiver are reported in Figure 9. The design of this test section has been aimed at developing a volumetric receiver that allows the evaluation of the optical capability of the considered nanofluid to absorb a high concentrated solar flux within its volume under realistic operating conditions. For this purpose, a computational fluid dynamic (CFD) model of the receiver presented in this paper has been developed in ANSYS Fluent® [39]. The results of the simulations were used to define the present geometry of the volumetric receiver, where two clear low-iron glass sheets, having a thickness of 3 mm, form the front (where the solar irradiance is concentrated) and the rear surfaces of the receiver. The glass on the rear part of the channel is used to trap only the solar radiation absorbed by the nanofluid, and hence to allow the measurement of the heat gain due to the mere nanofluid optical absorption. Consequently, the geometry of the receiver is not optimized to maximize the energy efficiency of the collector.
Figure 9. Compact (a) and exploded (b) views of the volumetric receiver for direct absorption of solar concentrated irradiance.

The glass sheets are provided with an anti-reflective coating, to achieve high transmittance in the wavelength range between 300 nm and 2400 nm, which is the most interesting for solar thermal applications. A sample of the glass used in the receiver has been optically characterized. The resulting
spectral dependence of the glass transmittance is shown in Figure 10. The glass sheets are embedded in two stainless steel frames, which give mechanical stiffness to the full structure. A thin layer of PTFE is interposed between glass and frames, to protect the glass itself. The front steel frame has a thickness of 6 mm, while the rear steel frame is 10 mm thick to host the threads for the tube fittings for nanofluid inlet and outlet.

![Figure 10. Spectral transmittance characterization of the glass used in the test section.](image)

A modular structure in which two or three PEEK frames can be combined forms the side walls of the flow channel. This modular configuration allows varying the channel depth of the receiver between 12 mm (two PEEK frames) and 18 mm (three PEEK frames). The choice to use PEEK as the frame’s material is due to its excellent mechanical and chemical resistance properties up to 240°C and its good thermal insulation (the thermal conductivity is 0.25 W m⁻¹ K⁻¹). Inlet and the outlet semicircular chambers for the nanofluid are obtained by shaping the PEEK frames and are connected to two threaded holes in the stainless steel frame on the rear part of the receiver. A diffusor is interposed between the PEEK frames to cause a localized pressure loss which allows a uniform distribution of the nanofluid across the section of the flow channel. The nanofluid enters the receiver through the inlet section, accumulates in the semicircularly shaped chamber between the PEEK frames and passes through the diffusor before flowing along the channel where it gets exposed to the concentrated solar radiation and lastly exits from the receiver. A CFD analysis has been carried out in ANSYS Fluent® to find the optimal geometry of the diffusor in order to provide an even flow distribution in the receiver [39]. All the layers of the receiver are kept together by tightening several bolts and nuts on the stainless steel frames. Viton® fluoroelastomer chords have been placed between the glass sheets and the PEEK frames, and on the inlet and outlet connections to guarantee hydraulic sealing of the volumetric receiver. During the present tests with the aqueous suspension containing 0.02 g L⁻¹ of
SWCHNs, a channel depth of 18 mm has been adopted. This depth assures the extinction of more than 95% of the incident light under laboratory conditions.

In order to minimize the incidence angle of the concentrated beams, the front surface of the flat receiver is tilted at 45° to the plane containing the focal line and the vertex line of the parabolic trough. The width of the absorber front surface is equal to 64 mm to achieve an intercept factor of 98%, which is a typical value in the current commercially available parabolic troughs [40]. The intercept factor for the present solar concentrator has been experimentally measured by mapping the concentrated solar flux on the focal region, according to the procedure illustrated in [41]. This optical analysis shows that increasing the width of the absorber further than 64 mm does not ensure any benefits in terms of the amount of intercepted concentrated beams on the receiver front surface. Furthermore, the bigger the absorber width, the higher the thermal losses towards the external surroundings. The resulting geometrical concentration ratio of the solar collector is equal to 46 but a peak value of the concentrated solar flux around 100 kW m\(^{-2}\) is expected on the focal line at a direct normal irradiance of 900 W m\(^{-2}\), according to the experimental analysis [41]. The length of the glass window is set to 500 mm to allow operating pressure up to 2.5 bar. Nevertheless, this limited length permits to collect sufficient radiative thermal power in order to be measured by means of the nanofluid temperature difference between inlet and outlet of the receiver with a low measurement error. The receiver is placed in the central section of the first mirrors row of the parabolic trough. This position assures that the front window of the receiver is exposed to the most uniform concentrated solar radiation along the flow channel length because its distribution is not affected by border effect. The receiver is mounted on two vertical aluminum supports sustained by a horizontal bar parallel to the focal line of the parabolic trough concentrator. The ends of the receiver's front steel frame are equipped with reflecting aluminum layers to avoid any contribution of solar flux absorption (Figure 11). The support structure is placed to avoid any shadow on the reflecting surface of the concentrator.
3.3 Test circuit

The test facility includes a primary loop arranged on board the concentrating collector and a secondary cooling loop (Figure 8). Both loops are thermally insulated by a 13 mm thick extruded elastomeric foam to limit heat losses towards the surroundings. The pipes and the instrumentations on board the collector are shielded from the concentrated solar beams that can strike them during the initial positioning. In the primary loop (Figure 8), after exiting the receiver, the nanofluid enters a tube-in-tube heat exchanger that acts as a heat sink: the heat flow rate provided by the concentrated solar irradiance is taken away by a secondary water flow. A parallel pipe with a regulation valve is included to eventually bypass the heat exchanger and reduce the heat transfer from the nanofluid to the secondary loop for operation at temperatures higher than 100°C. Afterward, the nanofluid is sent to an independently controlled rotary vane pump (Nuert PR4ASXV) magnetically coupled to a variable speed electric motor. This pump is used to set the mass flow rate, which is measured by a Coriolis effect mass flow meter (Siemens SITRAN FC MASS2100). The pressure of the primary loop is regulated by a hydropneumatic accumulator with a fluoroelastomer membrane. Before entering the receiver, the nanofluid passes through a pre-heating section which consists of a heating wire wrapped around a stainless steel tube. The electrical heater is connected to a solid state relay which is governed by a PID temperature controller. The PID controller uses a T-type thermocouple as a probe to monitor the trend of the external wall temperature of the stainless steel pipe downstream of the pre-heating section. Three high precision absolute pressure transmitters (STS ATM.1ST) have been connected to the primary loop pressure taps to gauge the pressure at the inlet and outlet of the receiver and at the
outlet of the tube-in-tube heat exchanger. The temperatures of the nanofluid at inlet and outlet of the receiver and downstream of the heat exchanger are measured by Pt100 resistance temperature detectors (RTDs). A vent valve sits at the highest point of the primary loop to eventually remove the non-condensable gases trapped in the circuit.

In the secondary cooling loop (Figure 8), the water coming from the tube-in-tube heat exchanger enters a first storage and passes through a plate heat exchanger, where the heat gained from the primary loop is wasted to the ground water of the building central plant. Afterward, the cooling water enters a second storage that is provided with four electrical heaters. The controls on the secondary mass flow rate and inlet temperature are useful to achieve constant conditions of the primary working fluid at the inlet of the receiver.

A first class Kipp&Zonen CHP1 pyrheliometer mounted on a high precision EKO Instruments STR-22G solar tracker is used to measure the direct normal irradiance (DNI). Finally, an anemometer measures the wind speed on the horizontal plane and the ambient air temperature is gauged by a Pt100 RTD. An Agilent 34970A Data Acquisition / Data Logger Switch Unit registers the electrical signal coming from the sensors and transmitters with a sampling rate of 3 seconds.

4. Experimental methods and data reduction

4.1 Experimental procedure

The thermal performance of a solar collector is usually presented in a diagram where the thermal efficiency is plotted as a function of the reduced temperature difference $T_m^*$ (Equation 1).

$$T_m^* = \frac{\left( T_{out,R,I} + T_{in,R,I} \right)}{2} - T_{amb} = \frac{T_{m,R,I} - T_{amb}}{DNI}$$ (1)

In Equation 1, $T_{in,R,I}$ and $T_{out,R,I}$, are the inlet and outlet temperatures of the nanofluid, $T_{amb}$ is the ambient air temperature and DNI is the direct normal irradiance. The overall thermal efficiency of a concentrating solar collector $\eta_{col}$ in which a working fluid is heated, is defined according to Equation 2:

$$\eta_{col} = \frac{\dot{q}_{th}}{DNI A_{ap}} = \frac{\dot{m}_I c_I (T_{out,R,I} - T_{in,R,I})}{DNI A_{ap}}$$ (2)

where $c_I$ is the isobaric specific heat capacity of the working fluid at the mean temperature between inlet and outlet of the receiver and $A_{ap}$ is the aperture area of the concentrating collector. In the present work, data collection and data reduction have been performed according to the quasi-dynamic test method described in the European Standard EN ISO 9806:2013 [42].

Before the test campaign, the nanofluid with a SWCNHs concentration of 0.02 g L$^{-1}$ has been kept at ambient temperature in a tank protected by sunlight. The primary loop is evacuated and then it is
filled with the nanofluid by using a centrifugal pump. The residual air content is removed by circulating the nanofluid at high mass flow rate while keeping the vent valve open. Experimental test runs were conducted at a nanofluid mass flow rate of about 350 kg h\(^{-1}\), which allows to a transition flow regime in the receiver. Working with lower mass flow rates leads to a higher residence time of the nanofluid in the receiver and to an increased mean temperature. Furthermore, a laminar flow regime may cause a significant temperature gradient across the front glass windows and thus increases the risk of cracks formation in the glass induced by thermal stresses.

When performing liquid heating tests, a preconditioning period of 20 minutes has been observed as indicated in the standard [42]. During each test sequence, the measured data are averaged every 5 minutes: in other words, each measured value in this work is the average value of 100 recordings while the collector is working under steady-state conditions, according to the specifications of EN ISO 9806:2013 [42].

Prior to the test, the distribution of concentrated solar flux has been experimentally defined using a solar flux mapping system including a water-cooled heat flux microsensor mounted on a semi-automatic two axes linear system. Further details on the test apparatus and the technique are illustrated in [41]. By using the experimental technique described in [41] and the measurement of the direct normal irradiance (DNI), it is possible to calculate the radiative power \(\Phi_{rec}\) incident on the front glass of the volumetric receiver from the DNI measured when testing the direct absorption concentrating collector. This parameter allows the definition of the receiver thermal efficiency (Equation 3), which represents the capability of the absorbing device in converting concentrated solar energy into useful thermal energy and it is independent on the optical and tracking characteristics of the solar concentrator.

\[
\eta_{rec} = \frac{\dot{q}_{th}}{\Phi_{rec}} = \frac{m_f c_f (t_{out,RJ} - t_{in,RJ})}{\Phi_{rec}}
\]  

All the measured quantities recorded by the data logger are reduced in a MathWorks MATLAB® ambient by calculating the fluid properties with NIST Refprop Version 9.0 [43].

### 4.2 Experimental uncertainty analysis

An uncertainty analysis has been performed in agreement with the guidelines provided by the "Guide to the Expression of Uncertainty in Measurement" [44]. Type A uncertainty arises from the statistical analysis of repeated observations and, in the present tests, it comes out considering 100 readings collected over the averaging time of 5 minutes. Type B uncertainties of the measured parameters considered in this work, result from calibration of instruments, calibration certificates, manufacturers' specifications and uncertainties assigned in reference handbooks. A list of the Type B uncertainties is reported in Table 1 (confidence level of 95%).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Uncertainty (confidence level 95%)</th>
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<tbody>
<tr>
<td>Ambient air temperature</td>
<td>± 0.1°C</td>
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Usually RTDs manufacturers provide a Type B uncertainty that depends on the measured temperature: for the present sensors, it is ±0.04°C at 5°C and ±0.1°C at 90°C. Nevertheless, in Table 1, the type B uncertainty of the RTDs in the primary loop is reported as a constant value of ±0.03°C, which is valid within the temperature range of the present tests. This value results from the calibration procedure performed using a high precision four wire RTD, that is calibrated up to 150°C. The reference RTD is connected to a Hart Scientific Super Thermometer II providing a measure chain with a global accuracy within ±0.01°C. The combined standard uncertainty of the parameters that are not directly measured can be calculated by applying the law of error propagation. The expanded experimental uncertainty is obtained by multiplying the relevant standard uncertainty by a coverage factor equal to 2, which corresponds to a level of confidence of 95%.

5. Results and discussion

5.1 Thermal efficiency tests

The experimental tests of the SWCNHs nanofluid with a concentration of 0.02 g L⁻¹ under concentrated solar radiation have been performed in clear-sky days in Padua, Italy (45° 24' 23" N, 11° 52 40" E). Two test sequences in two different days with an interval of one week have been carried out using the same working fluid. A total of 71 data points has been collected. During the first test day, the direct normal irradiance was between 920 W m⁻² and 960 W m⁻² and the ambient air temperature between 27°C and 29°C. The direct normal irradiance during the second test varied between 780 W m⁻² and 680 W m⁻² with an ambient air temperature around 36°C. The nanofluid in the primary loop has been maintained at a mass flow rate close to 3.50 kg h⁻¹ for both test sequences and its temperature at the inlet of the receiver was equal to 33°C. The average difference between the mean temperature of the nanofluid and the ambient air temperature was 7 K and -2 K during the first and the second test sequences, respectively. That means that the collected data are only slightly affected by the heat losses, therefore the calculated collector thermal efficiencies are mostly affected by the optical efficiency of the present direct absorption concentrating collector.

Figure 12 depicts the volumetric receiver efficiency (see Equation 3) with the corresponding error bands against the exposure time of the nanofluid under concentrated solar irradiance. The expanded experimental uncertainty on the receiver efficiency ranges between ±3.5% and ±5.5%.

The time in the horizontal axis of Figure 12 represents the actual exposure time of the nanofluid to the concentrated solar radiation. During the first test day, the receiver efficiency did not vary significantly and a maximum value of 82% has been achieved. This efficiency is lower than what was expected from the optical characterization tests on the nanofluid performed in laboratory (Figure 5).
A plausible reason for this could be the saturation of absorption in the nanofluid at high incident intensities. This phenomenon has been recently checked at two discrete wavelengths in the green and infrared regions, finding that SWCNHs show a nonlinear optical effect at higher energy densities than the radiative flux measured in the present experiment. However, no indication so far is available regarding the optical effect at high radiative intensity in the whole solar spectrum. Another possible explanation may be addressed to some kind of instability of the nanofluid due to the mere circulation in the apparatus. Unfortunately, no information can be obtained from the available analysis.

From Figure 12, a continuous decrease of the performance of the nanofluid-based device during the second test day can be seen. After eight hours under solar concentrated radiation, the receiver efficiency was equal to 65%. This result clearly indicates that a progressive degradation of the optical properties occurs when the nanofluid is exposed at high concentrated solar flux. The degradation of the absorption capacity of the nanofluid is due to the instability of the SWCNHs suspension in the present concentrating collector. In fact, when monitoring the aspect of the nanofluid inside the receiver channel during the experimental campaign, the change in the working fluid aspect indicates a variation of the nanoparticles concentration due agglomeration and precipitation phenomena.

![Graph](chart.png)

**Figure 12. Experimental receiver efficiency versus exposure time of the receiver under concentrated solar radiation (First test day: DNI 920 - 960 W m$^{-2}$, T$_{amb}$: 27-29°C; Second test day DNI: 680 - 780 W m$^{-2}$, T$_{amb}$: 35-38°C).**

5.2 Measurement on the nanofluid during tests

Figure 13 presents three pictures of the flow channel (volumetric absorber) taken respectively, at the beginning of the test campaign (before being exposed to the concentrated solar radiation), between the first and the second test day (exposure time 3 h) and at the end of the test campaign (exposure...
time 8 h). When taking these picture, samples of the bulk nanofluid has been collected in order to characterize the concentration of the SWCNHs in the aqueous solution. As can be observed on the top picture, which shows the initial conditions of the nanofluid with a nanoparticles concentration of 0.02 g L\(^{-1}\), the flow channel appears dark and opaque. In the central picture, the paper behind the receiver can be clearly seen and the colour of the nanofluid looks like a semi-transparent brownish liquid. The analysis of the corresponding sample reveals that this change in colour and transparency is due to the reduction of the SWCNHs concentration down to 0.01 g L\(^{-1}\). In the bottom picture, the nanofluid has lost almost completely its initial colour, resembling the aspect of pure water. The nanoparticles concentration of the sample corresponding to this last picture results equal to 0.004 g L\(^{-1}\). These concentrations of SWCNHs into suspension reported in Figure 13 have been estimated from the absorbance corresponding to the interband \(\pi\) plasmon peak at the wavelength of about 260 nm, typical of SWCNHs and other graphene-based nanostructures [45], as shown in Figure 14. The concentrations have been calculated using the Lambert-Beer law

\[
A = \varepsilon_\lambda \, l \, C
\]  

(4)

where \(A\) is the absorbance, \(\varepsilon_\lambda\) is the extinction coefficient, \(l\) is the beam path length and \(C\) is the concentration. Optical transmittance spectra at room temperature have been obtained using a double-beam UV–vis spectrophotometer (Perkin Elmer Lambda 35) from 200 nm to 1100 nm wavelength. The SWCNHs suspensions have been held in quartz cuvettes, with 1 mm beam path length.

Exposure time = 0 h  
(Concentration 0.02 g L\(^{-1}\))

Exposure time = 3 h  
(Concentration 0.01 g L\(^{-1}\))

Exposure time = 8 h  
(Concentration 0.004 g L\(^{-1}\))

*Figure 13. Pictures of the nanofluid volume in the flow channel of the receiver taken at different exposure times.*
A possible explanation for the observed instability of the SWCNHs suspension is the rapid degradation of the polymeric surfactant when exposed to the highly concentrated solar radiation. Another possibility is the irreversible desorption of surfactant molecules from the surface of nanoparticles due to the local overheating. Both mechanisms can lead to a decreased \( \zeta \)-potential of the suspension due to the loss of charge on the surface of nanoparticles, besides to the loss of steric stabilization, and thus to the agglomeration of the SWCNHs. DLS measurements after the test runs revealed that the average size of aggregates shifted from 143 nm for the original suspension to 95 nm and 81 nm after the first and second test day, respectively. This means that the biggest aggregates or particles tend to coalesce and precipitate, thus not participating to radiation absorption into the collector. \( \zeta \)-potential measurements showed a reduction in absolute value from -44 mV to -35 mV and -32 mV after the first and second test day, respectively. This trend could be a hint of surfactant degradation during the exposure to concentrated solar radiation. In parallel, it is not clear how the fluid circulation can contribute to the aggregation of the nanoparticles.

5.3 Comparative results

Beyond the encountered stability issue, the initial performance of the volumetric receiver is very promising. In Figure 15, a comparison between the performance achieved using the present volumetric receiver and a flat bar-and-plate surface-absorption receiver [2] mounted on the same asymmetrical parabolic trough is reported. The plot shows the overall collector experimental thermal efficiencies (see Equation 1) against the reduced temperature difference. Furthermore, the efficiency curve for the concentrating collector including the bar-and-plate surface absorption receiver is also depicted (dashed line). In the present tests with the volumetric receiver, the reduced temperature difference was between -0.006 K m\(^2\) W\(^{-1}\) and 0.009 K m\(^2\) W\(^{-1}\). The expanded experimental uncertainty...
on the thermal efficiency ranges between ±2.8% and ±4.9% while the maximum expanded experimental uncertainty on the reduced temperature difference is of ±0.0003 K m$^2$ W$^{-1}$.

Figure 15. Comparison of experimental thermal efficiencies of parabolic trough collector using the present volumetric receiver (red circles and blue diamonds) against the same collector using a surface receiver and water as the working fluid (yellow triangles).

Figure 15 shows that the two systems present the same thermal efficiency at 0.0075 K m$^2$ W$^{-1}$. This corresponds to the average reduced temperature difference during the first test campaign. As mentioned in Section 3.2, the design of the volumetric receiver was not aimed to maximize the photothermal conversion efficiency, thus there is margin to increase the values of the thermal efficiency of the present DASC. For example, by replacing the glass on the rear of the receiver with a reflective material and an insulation layer.
6. Conclusions

A low-cost nanofluid containing 0.02 g L\(^{-1}\) of SWCHNs in distilled water was prepared and its thermal and optical properties were characterized. Sodium dodecyl sulphate was added as surfactant to achieve stability under laboratory conditions. The nanofluid optical capability to absorb high concentrated solar fluxes has been experimentally investigated using this suspension as working fluid and volumetric absorber in a parabolic trough direct absorption solar collector.

Tests have been performed according to a standardized procedure with the nanofluid flowing in an ad-hoc designed receiver at 83.4 kg m\(^{-2}\) s\(^{-1}\) specific mass flow rate and temperature close to that of the ambient air to minimize the effect of the heat losses. The nanofluid flow channel is 18 mm deep, displaying glass windows both on the front and on the rear of the receiver.

During the first two hours of exposure to concentrated solar radiation, the receiver thermal efficiency did not vary significantly and reached 82%. After that, a continuous decrease in the efficiency of the direct absorption receiver was found, down to 65% after 8 hours of exposure. Furthermore, a change in colour and transparency of the nanofluid in the receiver was observed.

Spectrophotometric analysis on specimens of bulk nanofluid taken at different exposure times revealed that the concentration of SWCNHs decreases due to coalescence and precipitation of the biggest aggregates. After 3 hours of exposure, the SWCNHs concentration in water was halved and, after 8 hours, it was of 0.004 g L\(^{-1}\). The observed instability may be explained by a rapid degradation of the polymeric surfactant or an irreversible desorption of surfactant molecules from the surface of nanoparticles under concentrated solar flux. The fluid circulation may also contribute to the nanoparticles aggregation.

In order to characterize the performance of the volumetric receiver, it was compared to previous data obtained with a surface absorber. Although the geometry of the receiver was designed for testing and not optimized for thermal efficiency, the initial performance of the volumetric receiver was similar to that of a surface receiver, using a flat bar-and-plate with an inner turbulator and mounted on the same parabolic trough concentrator. Thus, the present results demonstrate that there is much room for further improvements.
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Nomenclature

Acronyms

- CFD: Computational Fluid Dynamics
- DASC: Direct Absorption Solar Collector
- DLS: Dynamic Light Scattering
- FE-SEM: Field Emission – Scanning Electron Microscopy
- PEEK: PolyEtherEtherKetone
- PTFE: PolyTetraFluoroEthylene
- RTD: Resistance Thermal Detector
- SDS: Sodium Dodecyl Sulfate
- SWCNH: Single Wall Carbon Nanohorn

Symbols

- $A$: Absorbance
- $A_{ap}$: Aperture area of the concentrating collector, m$^2$
- $C$: Concentration, mol cm$^{-1}$
- $c_l$: Isobaric specific heat capacity of the nanofluid, J kg$^{-1}$ K$^{-1}$
- $DNI$: Direct Normal Irradiance, W m$^{-2}$
- $l$: Beam path length, cm
- $\dot{m}_l$: Nanofluid mass flow rate, kg s$^{-1}$
- $\dot{q}_{th}$: Heat flow rate, W
- $t$: Exposure time, h
- $T_{amb}$: Ambient air temperature, K
- $T_m^*$: Reduced temperature difference, K m$^{-2}$ W$^{-1}$
- $T_{in \, R,I}$: Working fluid temperature at the receiver inlet, K
- $T_{out \, R,I}$: Working fluid temperature at the receiver outlet, K

Greek symbols

- $\varepsilon_\lambda$: Spectral extinction coefficient
- $\eta_{col}$: Thermal efficiency of the concentrating collector
- $\eta_{rec}$: Thermal efficiency of the receiver
- $\Phi_{rec}$: Incident radiative power, W
References


