

**BLACK NANOFLUIDS FOR SOLAR ABSORPTION ON  
THE BASIS OF HYDROGEN PEROXIDE  
TREATED CARBON PARTICLES**

Rumen Kirilov<sup>1</sup>, Christian Girginov<sup>2§</sup>, Petko Stefchev<sup>3</sup>

<sup>1,3</sup>Laboratory for Solar Energy and New Energy Sources  
72, Tzarigradsko Chaussee Blvd., 1784, Sofia, BULGARIA

<sup>2</sup>Department of Physical Chemistry  
University of Chemical Technology and Metallurgy  
8, St. Kliment Ohridski Blvd., 1756, Sofia, BULGARIA

**Abstract:** In this study the effect of carbon black nanoparticles concentration in water and propylene glycol based nanofluids on the solar energy absorbance has been studied. These nanofluids have been obtained by preliminary treatment of the used carbon particles with H<sub>2</sub>O<sub>2</sub>, heating and magnetic stirring. This pretreatment alters their wettability, sticking and surface adsorption, which permits the producing of stable nanofluids. Transmittance and extinction coefficients of these carbon black nanofluids have been estimated in the visible range. The optimal concentration of the carbon particles (0.2 g dm<sup>-3</sup>) for both dispersion media has been determined. The extinction coefficients for water-based fluids are slightly higher than those for the propylene glycol based ones. Their values slightly decrease with wavelength. Solar transmittance mean values in the visible spectrum indicate that the investigated fluids have a high potential for solar energy conversion. Such a good efficiency has also been established for solar radiation absorption in a wider wavelength range (200-2500 nm). Photothermal experiments of the studied carbon black nanofluids show a good temperature increase rate with solar irradiation time.

**Key Words:** carbon black nanofluids, stability of fluids, transmittance, extinction coefficients, photothermal properties

---

Received: August 9, 2013

© 2013 Academic Publications, Ltd.  
url: [www.acadpubl.eu](http://www.acadpubl.eu)

<sup>§</sup>Correspondence author

## 1. Introduction

In conventional solar thermal collectors, plates or tubes coated with a layer of selectively absorbing material are used to absorb solar energy, and then this energy is carried away in the form of heat by working fluids [1-3]. This type of collector exhibits several shortcomings, such as limitations on incident flux density and relatively high heat losses [4]. In this case the efficiency is limited by not only how effectively the absorber captures solar energy but also how effectively the heat is transferred to the working fluid. In order to overcome these drawbacks, direct solar absorption collector has been used for solar thermal utilization. In this type of collectors, sunlight is absorbed directly from the working fluid and is then exported in the form of heat. In the last century, black liquids (suspensions) containing nanometer to micrometer-sized particles were used as working fluids in solar collectors due to their excellent photothermal properties [5].

However, the applications of these black nanofluid (BNF) suspensions are limited because of severe abrasion, sedimentation, and plug problems of coarse particles. Nevertheless, nanofluids find increasing implementation as working fluids in direct solar collectors [6-9]. Several researchers have reported that nanofluids could effectively improve solar energy utilization [10, 11]. Taylor et al [12] found nanofluids had excellent potential for solar thermal power plants. Efficiency improvement in the order of 5% to 10% was possible with a suspension receiver. Carbon black is a kind of material that has very good absorption in the whole sunlight wavelength range [7]. Carbon black nanofluids seem to have a high potential in the application of solar utilization. Nanoparticle carbon materials have been added to different base fluids and characterized in terms of their performance for improving heat transfer efficiency. Some liquids (see [13]) such as water, ethylene glycol, propylene glycol (see [14]) and oils are commonly used as dispersion media. The photothermal properties of nanofluids, used for direct absorbers are essential for solar energy utilization, because they directly reflect the nanofluids' absorption abilities.

In this study, carbon black nanofluids were prepared by dispersing the pretreated carbon black powder into distilled water and propylene glycol. The optical and photothermal properties of these nanofluids were investigated with the intention to be used in solar heat collectors.

## 2. Experimental

For the nanofluids preparation commercial carbon black powder (N115), supplied by Degussa, was used. To obtain stable nanofluids, the carbon powder was pretreated: 7.5 g of carbon powder and 200 ml  $H_2O_2$  (30%) were mixed into a flask and boiled under magnetic stirring for 4 h. Then additional 200 ml  $H_2O_2$  were added and the solution was further stirred and boiled for another 4 hours and finally it was diluted with distilled water to 300 ml. Hydrogen peroxide reacts on the carbon surface, and undergoes decomposition to oxygen and water. The reaction of oxygen with carbon surfaces has two main effects: activation of molecular oxygen on the surface and stabilization of activated species by formation of covalent bonds with carbon atoms. The oxidation of

carbon significantly alters its physicochemical properties, such as wettability, sticking and surface adsorption, which contributes to the producing of stable nanofluids. Two types of nanofluids with various concentrations of carbon particles were prepared, using this base solution, by diluting it with distilled water (W) and propylene glycol (PG). When diluting with PG, its content is 90% of the nanofluid volume.

Transmittance spectra were recorded in the visible range (400 - 800 nm) with a spectrophotometer, using cuvettes with optical length path of 0.01 dm. The optical measurements were performed by recording absorbance spectra at normal incidence in the UV–VIS–NIR range (200 to 2500 nm) by Shimadzu UV3100 with BaSO<sub>4</sub> integrating sphere (total near-normal reflectance was measured relative to a BaSO<sub>4</sub> reference). A scheme of the employed photothermal test equipment is presented in Figure 1. Carbon black nanofluids (BNF) were sealed in soda lime glass tubes (d = 17 mm, h = 160 mm).

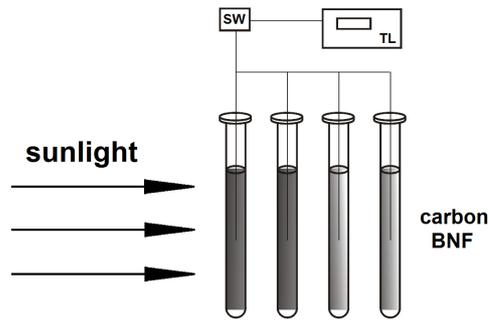


Figure 1: Experimental setup: SW-signal switch, TL-temperature logger [15]

The tubes were placed in an insulation box, where the insulation materials were put under and between the tubes. Each tube was filled with the same amount of nanofluid, so that each specimen has the same heat transfer area. The nanofluid temperature was measured and recorded in real time using thermocouples. Experiments in direct sunlight were carried out in two series and the obtained results have been averaged.

### 3. Results and Discussion

#### 3.1. Stability of the Fluids

In order to determine the thermal stability of the fluids, the Rayleigh numbers have been calculated using the samples' diameter as characteristic length and temperature difference of 1°C. Rayleigh numbers were 23 000 and 14 000 for water and propylene glycol based nanofluids, respectively. Following the method described in [16] it can be concluded that the nanofluids are in the instability region and it is expected natural convection to take place. As a result it can be supposed that the sample has almost uniform temperature and measuring the temperature at one point is representative.

### 3.2. Transmittance and Extinction Coefficients

The transmittance of the investigated nanofluids can be represented by the law of Bouguer-Lambert-Beer:

$$T = \frac{I}{I_0} = 10^{-\alpha l} = 10^{-\varepsilon l C}, \quad (1)$$

where  $T$  is transmittance,  $I_0$  and  $I$  are intensity of the incident and transmitted light respectively,  $l$  is the length path,  $\alpha$  is the absorption coefficient of the substance,  $\varepsilon$  is the molar specific extinction coefficient of the light calculated per unit concentration ( $C$ ) of the substance determining the absorption.

The transmittance in the visible spectrum for different carbon nanoparticle concentrations is presented in Figure 2 (water based nanofluid) and Figure 3 (propylene glycol based nanofluid).

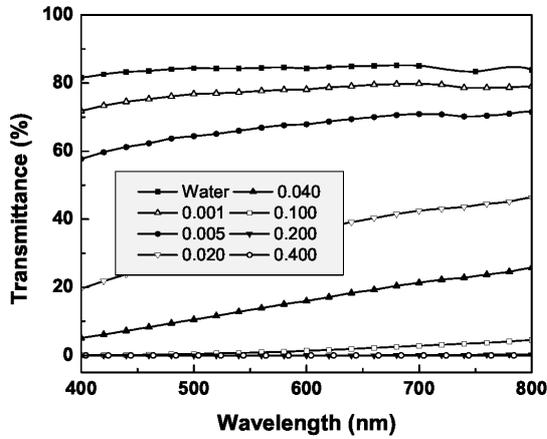


Figure 2: Spectral transmittance of water (W) based nanofluids with different carbon concentrations ( $\text{g dm}^{-3}$ ).

It is worth noting that the transmittance decreases strongly with increasing concentration of carbon particles. Minimal values have been achieved at a concentration of the carbon particles  $\geq 0.2 \text{ g dm}^{-3}$ . For the calculation of the extinction coefficients ( $\varepsilon$ ) the logarithmic form of the Bouguer-Lambert-Beer was used:

$$-\log \frac{I}{I_0} = -\log T = \alpha l = \varepsilon l C. \quad (2)$$

These dependencies for the investigated nanofluids based on both dispersion media, are presented in Figure 4 (water) and Figure 5 (propylene glycol).

From the slopes of the  $-\log(I/I_0)/C$  - curves the extinction coefficients ( $\varepsilon$ ) have been calculated at three different wavelengths within the visible spectrum. These

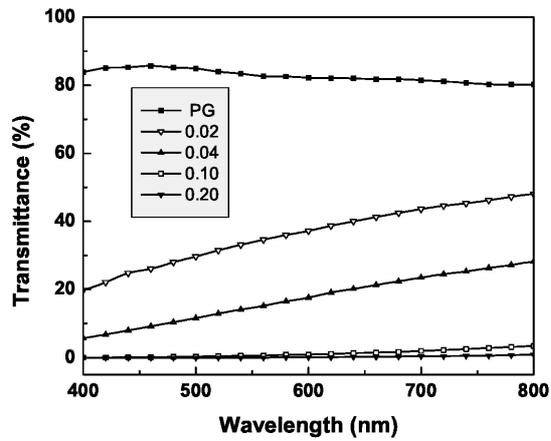


Figure 3: Spectral transmittance of propylene glycol (PG) based nanofluids with different carbon concentrations ( $\text{g dm}^{-3}$ ).

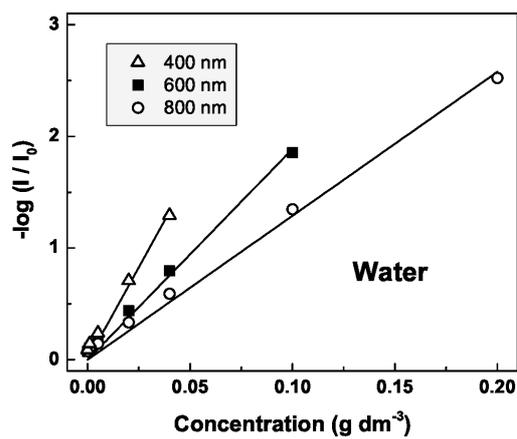


Figure 4:  $-\log(I/I_0)/C$  dependencies for water (W) based nanofluids at three wavelengths: 400 nm, 600 nm and 800 nm.

calculations are done for a cuvette with a length path of 0.1 dm. The results have been summarized in Table 1.

The extinction coefficients for water-based fluids are slightly higher than those for the propylene glycol based ones. Their values slightly decrease with wavelength, which

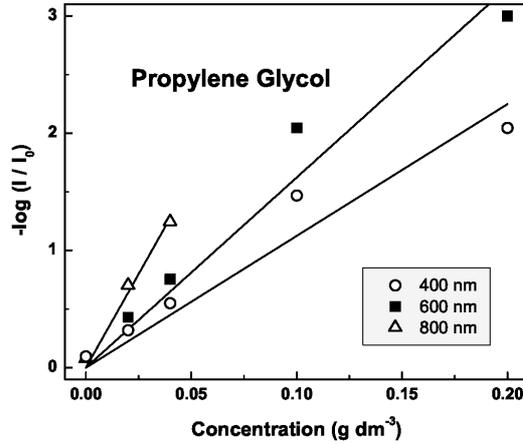


Figure 5:  $-\log(I/I_0)/C$  – dependencies for propylene glycol (PG) based nanofluids for wavelengths: 400 nm, 600 and 800 nm.

$\lambda$ [nm]	Extinction coefficient, $\varepsilon$ [ $\text{g}^{-1} \text{dm}^2$ ]	
	Water (W)	Propylene glycol (PG)
400 nm	331.6	319.2
600 nm	188.7	162.2
800 nm	128.9	112.4

Table 1: Carbon black nanofluid extinction coefficient.

is common to most black nanofluids, obtained on the basis of carbon particles.

### 3.3. Solar Transmittance Mean Values

Mean values of the solar transmittance ( $\tau$ ) in the visible wavelength range were calculated in accordance with the European Standard EN 410 (1998):

$$\tau = \sum_{i=1}^n S_i \Delta\lambda \quad (300 - 2500 \text{ nm}), \quad (3)$$

where  $S_i$  designates solar intensity in the corresponding bandwidth  $\Delta\lambda$  tabulated in EN 410, and  $\tau$  is the internal transmittance of the sample at specified  $\lambda$ .

The obtained results in the range (400 - 800 nm) for the studied concentrations of carbon particles for both dispersion media (water and propylene glycol) are presented in Table 2.

Dispersion medium			
Water (W)		Propylene glycol (PG)	
Concentration [g dm <sup>-3</sup> ]	Transmittance $\tau(\lambda)$ [%]	Concentration [g dm <sup>-3</sup> ]	Transmittance $\tau(\lambda)$ [%]
0.001	77.31	-	-
0.005	65.83	-	-
0.020	33.41	0.02	34.21
0.040	14.12	0.04	15.11
0.100	1.30	0.10	0.92
0.200	0.02	0.20	0.13
0.400	0.00	0.40	0.00

Table 2: Calculated mean values for nanofluid transmittance in the interval 400-800 nm.

It is known that 60% of the solar energy reaching the Earth's surface is carried by irradiation having wavelengths from 350 to 850 nm. This gives grounds to assume that the results are representative for the entire solar spectrum.

Additional experiments with carbon particle concentration of 0.2 g dm<sup>-3</sup>, based on both water and propylene glycol, have been conducted. The optical measurements were done by recording solar absorbance spectra at normal incidence in the UV-VIS-NIR range (200 to 2500 nm). The obtained results demonstrate a solar absorbance of over 96% in both dispersion media.

### 3.4. Photothermal Properties of Carbon Black Nanofluids

The temperature dependence of carbon black nanofluids as a function of solar irradiation time is presented in Figure 6. Experiments were carried out with 0.2 g dm<sup>-3</sup> carbon particles concentration, starting from the initial temperature of 25°C. For comparison the same dependencies for pure dispersion media (W and PG) are also plotted.

It can be seen that the temperature of the nanofluids increase more quickly than water and propylene glycol alone. The addition of carbon particles logically improves the solar thermal energy absorption properties. The temperature increase enhancement of carbon black nanofluids is higher than that of TiO<sub>2</sub>/water, SiO<sub>2</sub>/water, and ZrC/water nanofluids [13, 14]. This proves once more that these fluids are a good medium for the absorption of solar energy.

Carbon particles absorb almost all solar energy in the volume of nanofluid and disseminate it to the surrounding medium. Water exhibits improved thermal conductivity compared to propylene glycol, which accounts for the more rapid heating of the water based fluid. It is clear that these nanofluids are suitable for use at temperatures up to 90°C at atmospheric pressure. In cases where higher temperatures or pressure are needed, it is necessary to use a propylene glycol medium, because of its higher boiling point.

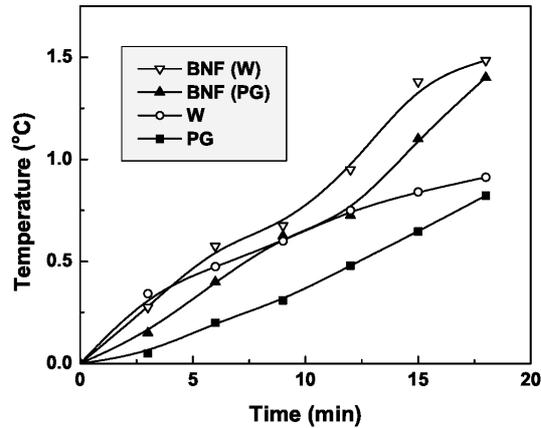


Figure 6: Temperature of carbon black nanofluids vs. solar irradiation time: BNF based on water (W) and propylene glycol (PG), pure water (W) and propylene glycol (PG).

#### 4. Conclusions

The pretreatment of carbon nanoparticles with hydrogen peroxide (by heating and magnetic stirring) results in surface activation and improvement of their physical and chemical properties, in terms of adsorption and wettability. Stable nanofluids can be obtained by dispersion of these pretreated particles in a water and propylene glycol medium. Transmittance and extinction coefficients of these carbon black nanofluids have been estimated in the visible range, which demonstrate good efficiency towards solar energy conversion. The calculated solar absorption in the wavelength range 200-2500 nm is over 96 % for the determined optimal carbon particle concentration of  $0.2 \text{ g dm}^{-3}$  for both types of black nanofluids. These results are somewhat better than those for nanofluids based on particles of other substances, such as  $\text{TiO}_2$ ,  $\text{SiO}_2$ ,  $\text{ZrC}$  etc. The photothermal properties of the investigated carbon black nanofluids show a sufficiently good temperature grow rate with solar irradiation time. The characteristics and test measurements of the developed nanofluids, based on water and propylene glycol, indicate their suitability for low and high medium temperature solar collectors.

#### Acknowledgments

The authors are grateful for the financial support of European Social Fund, Human Resources Development Programme, under the contract BG 051PO001-3.3.06-0014.

### References

- [1] T.P. Otanicar, J.S. Golden, Comparative environmental and economic analysis of conventional and nanofluid solar hot water technologies, *Environ. Sci. Technol.*, **43** (2009), 6082-6087.
- [2] L.J. Mu, Q.Z. Zhu, L.L. Si, Radiative properties of nanofluids and performance of a direct solar absorber using nanofluids, In: *2-nd ASME Micro/Nanoscale Heat & Mass Transfer International Conference*, **1** (2010), 549-553.
- [3] J.E. Minardi, H.N. Chuang, Performance of a black liquid flat-plate solar collector, *Sol Energy*, **17** (1975), 179-183.
- [4] H. Tyagi, P. Phelan, R. Prasher, Predicted efficiency of a low-temperature nanofluid-based direct absorption solar collector, *J. Sol. Energy Eng.*, **131** (2009), 041004, doi:10.1115/1.3197562.
- [5] J.E. Minardi, H.N. Chuang, Performance of a black liquid flat-plate solar collector, *Sol. Energy*, **17** (1975), 179-183.
- [6] R. Bertocchi, J. Karni, A. Kribus, Experimental evaluation of a non-isothermal high temperature solar particle receiver, *Energy*, **29** (2004), 687-700.
- [7] T.P. Otanicar, P.E. Phelan, J.S. Golden, Optical properties of liquids for direct absorption solar thermal energy systems, *Sol. Energy*, **83** (2009), 969-977.
- [8] C.H. Shou, Z.Y. Luo, T. Wang, J.C. Cai, J.F. Zhao, M.J. Ni, K.F. Cen, Research on the application of nano-fluids into the solar photoelectric utilization, *Shanghai Electric Power*, **16** (2009), 8-12.
- [9] T.P. Otanicar, P.E. Phelan, R.S. Prasher, G. Rosengarten, R.A. Taylor, Nanofluid-based direct absorption solar collector, *J. Renewable and Sustainable Energy*, **2** (2010), 033102.
- [10] H. Tyagi, P. Phelan, R. Prasher, Predicted efficiency of a nanofluid-based direct absorption solar receiver, In: *Proceedings of the Energy Sustainability Conference* (2007), 729-736.
- [11] L.B. Mao, R.Y. Zhang, X.F. Ke, The photo-thermal properties of coppernanofluids, *Journal of Guangdong University of Technology*, **25** (2008), 13-17.
- [12] R.A. Taylor, P.E. Phelan, T.P. Otanicar, C.A. Walker, M. Nguyen, S. Trimble, R. Prasher, Applicability of nanofluids in high flux solar collectors, *J. Renewable Sustainable Energy*, **3** (2011), 023104, doi:10.1063/1.3571565.
- [13] S.B. White, A.J. Shih, K.P. Pipe, Investigation of the electrical conductivity of propylene glycol-based ZnO nanofluids, *Nanoscale Res Lett.*, **6** (2011), 346.

- [14] R. Taylor, S. Coulombe, T. Otanicar, P. Phelan, A. Gunawan, W. Lv, G. Rosengarten, R. Prasher, H. Tyagi, Small particles, big impacts: A review of the diverse applications of nanofluids, *J. Appl. Phys.*, **113** (2013) 011301, doi:10.1063/1.4754271.
- [15] D. Han, Z. Meng, D. Wu, C. Zhang, H. Zhu, Thermal properties of carbon black aqueous nanofluids for solar absorption, *Nanoscale Research Letters*, **6** (2011), 457, doi:10.1186/1556-276X-6-457.
- [16] G.J. Sheard, M.P. King, Horizontal convection: Effect of aspect ratio on Rayleigh number scaling and stability, *Applied Mathematical Modelling*, **35** (2011), 1647-1655.