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An investigation of thermal stability of carbon nanofluids for solar thermal applications

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ABSTRACT

Carbon nanofluids are engineered materials with controllable thermal and optical properties. Stable, high temperature operation (> 20) of these fluids would enable them to improve upon – and eventually replace – pure fluids in many important commercial and industrial applications including applications in solar thermal collectors. To date, however, much of the nanofluids research focuses on low temperature (< 100 °C) applications and testing. For solar thermal collector applications, carbon nanofluids are uniquely well-suited due to their high absorptivity over the entire solar spectral range. This study pushes well beyond the 100 °C mark by conducting a range of experiments to identify appropriate base fluids and functionalization methods to produce stable carbon nanotube (CNT)-based nanofluid dispersions at temperatures of up to 250 °C to ensure their suitability for industrial heating applications (typically 100–250 °C). Different forms of CNTs including, single-walled carbon nanotubes, double-walled carbon nanotubes and multi-walled carbon nanotubes were chemically functionalized to obtain stable dispersions in water, glycol and Therminol (a synthetic heat transfer oil). The stability of chemically functionalized carbon nanotube dispersions at different temperatures, 20, 80, 100, 150, 200 and 250 °C, was investigated. The results of broadband UV–VIS–NIR spectroscopy showed no agglomeration in mildly oxidized multi-walled carbon nanotubes dispersed in Therminol when heated to 250 °C, highlighting this low-cost composite medium as a potential candidate for use in high temperature nanofluid-based solar thermal collectors.

1. Introduction

Nanofluids have increasingly attracted attention for use in solar thermal applications as materials which can be tailored to provide superior optical and thermos-physical properties [1]. Nanofluids are desirable for solar thermal application because they can serve as both the heat transfer fluid and as the solar absorber – efficiently converting sunlight to heat [2–8]. Typical heat transfer fluids used in conventional solar thermal collectors include water, molten salts and synthetic heat transfer fluids which are, for the most part, optically transparent [9,10]. By adding small amounts of nanoparticles (generally $\ll 0.1\%$ by mass), transparent fluids can be redesigned to absorb part, or all, of the solar spectrum [11–13].

As compared to conventional collectors, up to a 10% increase in the efficiency has been reported through the use of nanofluids [14–18]. The advantage of the direct absorption of solar thermal energy is that it avoids intermediate heat transfer steps and enables the highest temperatures to be generated inside the working fluid, rather than on the outside surface, which is typical of conventional surface-based solar thermal collectors [15,19–21]. Apart from taking advantage of the improved heat transfer configuration, volumetric absorption using nanofluids can be engineered to have extremely high solar-weighted absorbance (Fig. 1).

However, the instability of nanofluids at the elevated temperatures required for solar thermal applications and the resulting clogging of pumps and valves by agglomerated particles have limited the use of nanofluids to low temperature applications [16,19]. A number of nanoparticles, including carbon nanoparticles and metal nanoparticles have been investigated for use in solar thermal collectors [5,6,16,21–27]. It has been found that dispersing less than 0.1% volume fraction of nanoparticles can significantly enhance the solar radiation absorption capability of the base fluids by up to 7 orders of magnitude [5]. Amongst these particle options,

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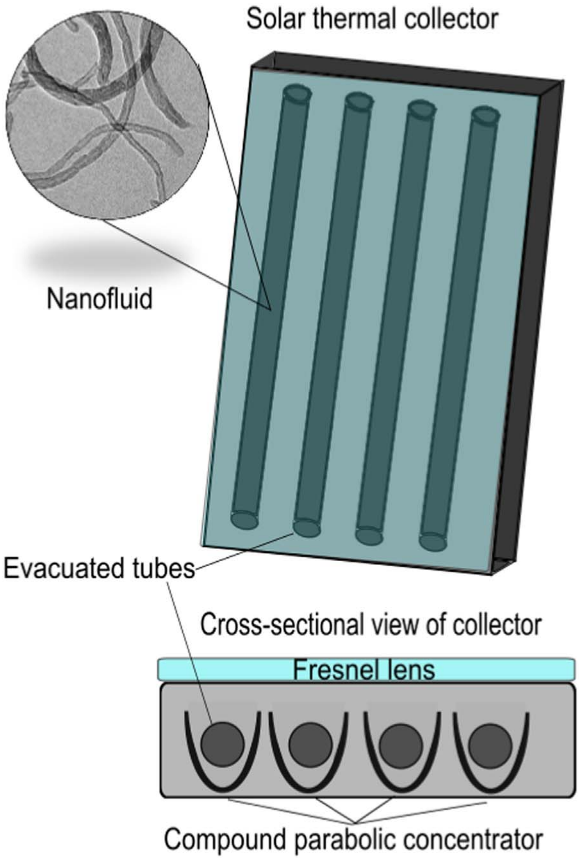

Fig. 1. A prototype nanofluid-based solar thermal absorber.

carbon-based materials, particularly carbon nanotubes (CNTs), provide the highest spectral absorptivity (particularly on a per unit mass basis) over the entire solar range [2,4]. Carbon nanotubes are present in different forms; single-walled carbon nanotubes (SWCNTs), double-walled carbon nanotubes (DWCNTs), and multi-walled carbon nanotubes (MWCNTs). SWCNTs are formed by wrapping a one-atom-thick layer of graphene into a seamless cylinder while DWCNTs and MWCNT are formed by concentrically wrapping two and multiple layers of graphite, respectively [28].

Although there remain many engineering issues to solve, CNTs are likely to play a central role in developing nanofluid-based solar thermal collectors [29–31]. To date, however, applications have been impeded by the low dispersibility of CNTs in base fluids [32,33]. Agglomeration of the CNTs in a nanofluid-based solar thermal collector will result in fouling, clogging, and a considerable reduction in the absorbance of incoming solar rays [30,34]. Dispersing CNTs in the base fluid is challenging due to their strong inter-particle interaction arising from Van der Waals interaction and their hydrophobic nature [35]. To date, a number of physical and chemical methods have been developed to achieve stable dispersions of CNTs [36–49]. Unfortunately, prior research on dispersion of nanotubes has focused predominantly on dispersion stability at temperatures that are considerably lower than those required in typical solar thermal collectors [30,34,50]. While physical methods, including ultra-sonication and the use of surfactants, can effectively disperse CNTs at low temperatures, the stability of the resulting dispersion has been found to decrease considerably as temperatures approach (or exceed) 100 °C [30,34,50,51]. Chemical functionalization has been also used widely in the literature to produce highly stable solutions at room temperature [52,53]. During chemical functionalization, functional groups (such as COOH, OH and COH) are attached to CNTs by treating nanotubes with strong oxidants such as sulfuric acid (H_2SO_4) and nitric acid (HNO_3) or by mild oxidation using potassium persulfate ($K_2S_2O_8$) [37,42,50,54–57]. However, the suitability of these methods is unknown for: i) dispersing CNTs in nonpolar solvents (e.g. glycols and heat transfer oils) and ii) maintaining a stable dispersion at elevated temperatures. These issues have not yet been fundamentally or systematically investigated. Developing stable CNT-based nanofluids for use in high temperature applications requires identifying the optimal combination of base fluid, type of CNTs, and dispersion agents (i.e. surfactants and/or functional groups) for the desired operating temperature range. To the best of our knowledge, no systematic study exists which investigates the thermal stability of different types of CNT solutions at the elevated temperatures. In the present study, the thermal stability of twenty seven different nanofluids was probed by varying: a) the type of CNTs (i.e. SWCNTs, DWCNTs and MWCNTs); b) the dispersion method (i.e. dispersion by surfactants, acid functionalization and base functionalization); and c) the type of base fluid (i.e. Therminol 55(TH55), propylene glycol (PG) and water). Thermal stability tests up to 250 °C were conducted to investigate the suitability of these nanofluids for use in high temperature applications. The main target temperature for this study was selected as 250 °C to ensure the suitability of nanofluids for industrial process heat applications (in the temperature range of 100–250 °C), a key emerging market for solar energy which is currently dominated by gas (and sometimes electricity) [58]. Additionally, due to importance of optical properties in solar thermal applications, UV–vis–NIR spectroscopy was used as a sensitive measurement of their stability, which is directly applicable to their optical property application in solar thermal collectors.

2. Experimental

2.1. Materials

Multi-walled carbon nanotubes and double-walled carbon nanotubes were purchased from Sigma Aldrich and used without further purification. Arc discharge single-walled carbon nanotubes (AP-SWCNTs) were purchased from Carbon Solutions, Inc. (Riverside, CA, USA). Therminol 55 and propylene glycol (PG) were purchased from Tru-Blu Oil Australia Pty Ltd. Nitric acid (HNO_3), sulfuric acid (H_2SO_4), potassium persulfate (KPS, $K_2S_2O_8$), potassium hydroxide (KOH) and sodium dodecylbenzenesulfonate (SDBS) were purchased from Sigma Aldrich and used without further purification.

2.2. Functionalization of CNTs

2.2.1. Chemical functionalization by acid treatment

Acid treatment has been shown to covalently graft oxygenated functionalities, such as carboxylic groups, onto the surface of CNTs. The acid functionalization approach used in this study involved adding 100 mg of each type of CNTs (SWCNTs, DWCNTs and MWCNTs) to 30 ml of a mixture of H_2SO_4 and HNO_3 in a volumetric ratio of 1:3 and stirring for 24 h at 90 °C. The acid treated CNTs were then collected by vacuum filtration using a polytetrafluoroethylene (PTFE) filter paper and washed repeatedly with water (8–10 times) until a pH of 6 was reached. The solids were then dried at 90 °C overnight.

2.2.2. Chemical functionalization by KPS

Under an alkaline condition, KPS oxidizes pristine nanotubes by introducing functional groups such as carboxylic potassium carboxylate (–COOK), carbonyl (–C=O) and hydroxyl (–C–OH) groups onto the surface of the CNTs. To achieve mild oxidization by KPS,