Thermal Stability and Conductivity of Carbon Nanotube Nanofluid using Xanthan Gum as Surfactant
(Kestabilan Termal dan Kekonduksian Bendalir Nano Karbon Tiub Nano menggunakan Gam Xantan sebagai Surfactan)

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ABSTRACT
A nanofluid is a suspension of nano-sized particles dispersed in a base fluid. It is very much obligatory to know more about stability and thermal characteristics of such a nanofluid for their further use in practical applications. In this research, multiwalled carbon nanotubes (CNT) is dispersed in water. CNT dispersed in water is highly unstable and it sediments rapidly due to the Vander Waals force of attraction. Therefore, to overcome this limitation, xanthan gum (XG) was added which behave as a promising dispersant followed by 4 h water bath sonication. Experimental work includes stability studies using UV-Vis spectroscopy with respect to CNT concentration (0.01 and 0.1 wt. %) and XG concentration (0.04 and 0.2 wt. %). The thermal conductivity of the most stable suspensions was measured using KD 2 Pro as a function of temperature (25-70°C) and CNT concentration. The optimum XG concentration was found for each CNT concentration studied. Thermal conductivity was observed to be strongly dependent on temperature and CNT concentration. The dispersion state of the CNT-water nanofluid is further examined using scanning electron microscope (SEM). In short, CNT nanofluids are found to be more suitable for heat transfer applications in many industries due to their enhanced thermal conductivity property. This work provides useful insight on the behavior of CNT nanofluids.

Keywords: Carbon nanotubes; nanofluid; stability; thermal conductivity; xanthan gum

INTRODUCTION
Several techniques have been suggested to increase the heat transfer performance of fluids in order to achieve smaller heat transfer systems with improved energy efficiencies and lower capital costs. Maxwell (1954) suggested utilizing micro-sized suspensions instead of common heat transport liquids due to higher thermal conductivity of solids compared to liquids. However, micro-sized particles pose many difficulties, such as higher pumping power requirement, sedimentation of particles and erosion of transport equipment. In order to overcome these limitations, ‘Nanofluid’ suspensions can be used that contains dispersed nano sized particles (Choi & Eastman 1995). Nanoparticles are very small particles (nanometer size) and based on the Stokes theory, nanofluids demonstrate higher stability than common suspensions. In addition the transport fluids require less pumping power and erosion effects compared to common suspensions. Moreover, nanofluids show much higher thermal conductivity compared to the base fluid and usual suspensions (Amrollahi et al. 2007; Choi & Eastman 1995; Keblinski et al. 2002; Wang & Mujumdar 2007; Wang et al. 1999; Yu et al. 2008). There are many parameters that affect the nanofluids behavior such as size and shape of
the particles, property of the base fluid and particles which are detailed in several studies (Ding et al. 2007; Liu et al. 2005; Zhang et al. 2007). However, the interactions among the various parameters have been neglected.

Besides, the stability of CNT based nanofluids is another major concern before utilizing in heat transfer equipment. It is reported that CNT based nanofluids are prone to sedimentation due to its hydrophobic nature, the high tendency of nanoparticles to agglomeration and its high aspect ratio (Garg et al. 2009; Hussein et al. 2013). In addition, other researchers (Ghadimi et al. 2011), specified that a durable and stable nanofluid is a key factor to achieve optimized thermal property performance. Ismail et al. (2016) investigated the rheological performance of multi walled carbon nanotubes in drilling fluids. They realized that applying xanthan gum with 0.2 wt. % as a surfactant improved rheological performance significantly (Ling et al. 2017) prepared non-Newtonian nanofluids by using xanthan gum (0.2 wt. %) and multi walled CNTs in order to enhance the shell-side heat transfer coefficient of the helical baffled heat exchanger. Interestingly, XG (0.2 wt. %) could improve heat transfer of multi walled carbon nanotubes. Also, Mahendran et al. (2012) reported that there is a relationship between stability and thermal conductivity of the carbon nanotube based nanofluids. Ponmani et al. (2014) xanthan gum (XG) prepared copper oxide and zinc oxide nanofluids with the use of Xanthan gum as a dispersant to enhance stability. They exhibited that copper oxide in 0.4 wt. % of xanthan gum was more stable than its counterpart.

In this present study, the focus was to enhance both the stability and thermal conductivity of CNT/water nanofluid. The stability of nanofluids is evaluated through visual method for duration of 2 months and also using UV vis spectroscopy method to determine the relative sedimentation with respect to time. XG is used as a surfactant to produce stable nanofluid samples. The thermal conductivity of nanofluids with the base fluid (water), XG solution and stable CNT nanofluids was investigated in this study.

**MATERIALS AND METHODS**

**EXPERIMENTAL DETAILS**

Multi-walled carbon nanotubes (MWCNTs) having an average O.D of 20-30 nm, I.D of, 5-10 nm, length of 10-30 μm and purity of 95% are obtained from Lab. Scientific, Malaysia. XG is obtained from the R & M Marketing; Essex, U.K. Distilled water is used in this research. Figure 1 shows the molecular structure of xanthan gum.

**PREPARATION OF NANOFLUID**

CNT of known mass is dispersed in water along with the measured amount of XG. The resultant suspensions were sonicated using water bath sonicator (Elma Transsonic TI-H-15, USA) at 50°C temperature for 4 h, frequency of 35 KHz. The sonication provides enough energy to detangle the CNT while the XG is adsorbed on the CNT surface preventing agglomeration and sedimentation. The diffusional rates and the frequency of collision between the individual tubes and XG molecule are achieved by sonication. It is important to know increased the temperature of water bath up to 80°C may change the properties of nanoparticles (Fadhillahanafi et al. 2013; Ponmani et al. 2014). According to literature, the optimum duration to maximize the adsorption of dispersant on the CNT is 4 h sonication time at 35 kHz (Rashmi et al. 2011). Also, reducing the aspect ratio of CNT and dislocation of carbon structure can be obtained by Prolonging sonication which will affect the thermal properties of CNT (O’Connell 2006).

**FIGURE 1.** Molecular structure of xanthan gum (Palaniraj & Jayaraman 2011)
CHARACTERIZATION

STABILITY
The stability of the Nanofluids usually has been determined by using UV-VIS spectroscopy (Shimadzu UV-1800, Japan). In this technique, after sonication of nanofluids, approximately 3 mL of sample was transferred instantly into the cuvette cells. Distilled water is used as blank sample for baseline correction, while reference sample (water + respective XG) was used to measure the CNT concentration with respect to time. Figure 2 clearly showed that the wavelength of CNT was 216 nm, which is in concordance with the applicable wavelength of the cuvettes (210 to 900 nm). Figure 3 demonstrates the absorbance value to carbon nanotube at various concentrations through the calibration curve. Based on the data in Figures 2 and 3, the optimum XG concentration for each CNT can be obtained through the graph of CNT concentrations versus sedimentation time.

The stability studies were carried out for two months, in order to investigate the most stable nanofluids. CNT concentration was measured with sediment time using UV-Vis spectrophotometer and stable nanofluids were determined with respect to CNT and XG concentration.

THERMAL CONDUCTIVITY
The thermal conductivity was measured based on the standard transient hot-wire method by utilizing a KD2-Pro thermal analyzer (Decagon Devices, USA). The transient hot wire (THW) method is a transient dynamic technique based on the measurement of the temperature rise of a linear hot wire embedded in the tested material. The wire (platinum) serves both as the thermometer and heating element. For a good measurement, the KS-1 needle is

FIGURE 2. UV Vis absorption spectrum of CNT in water

FIGURE 3. Calibration curve of light absorption and CNT concentration at 216 nm
immersed in a homogeneous medium with uniform initial temperature, heated with a constant heat flux per unit length and then the temperature rise \( T(t) \) of the wire is measured. Before measuring the thermal conductivity, the device was calibrated with glycerin. In order to avoid any convection errors and effects, it is essential to observe some important points such as preparing a thermally and acoustically stable environment around the sample and dipping the probe vertically into the middle of the suspension. It is significant to note that the KD2-Pro has the ability to indicate the quality of the measurement via an error factor. In order to have reliable thermal conductivity value the error should be less than 0.01. All measurements were repeated 10 times then the average value was reported, in order to confirm a precise measurement. 4 sets of nanofluid and XG solutions for each dispersant individually with different amount of CNT, XG are prepared and shown in Table 1.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Contents</th>
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<tbody>
<tr>
<td>1</td>
<td>Distilled water + 0.04 wt. % XG</td>
</tr>
<tr>
<td>2</td>
<td>Distilled water + 0.2 wt. % XG</td>
</tr>
<tr>
<td>3</td>
<td>CNT 0.01 wt. % + 0.04 wt. % XG + Distilled water</td>
</tr>
<tr>
<td>4</td>
<td>CNT 0.1 wt. % + 0.2 wt. % XG + Distilled water</td>
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SCANNING ELECTRON MICROSCOPY (SEM)

In order to investigate the morphological structure of CNT and its interaction with XG dispersant, the SEM (FEI Quanta 400F, USA) test was carried out. A small amount of samples (CNT 0.01 + XG 0.04 wt. %) and (CNT 0.1 + XG 0.2 wt. %) were transferred into the petri dish and dried overnight in an oven at 100°C before it is observed under SEM.

RESULTS AND DISCUSSION

It is recognized that CNT cannot be dispersed homogeneously in aqueous solution and thus form aggregation due to Van der Waals forces of attraction. Thus, the optimum amount of dispersant plays vital role to stabilize the CNT in aqueous solution. Studies on XG have been clearly showed that this biopolymer has a great capability being used as a surfactant in preparation of nanofluids. In this study, XG behaves as a suitable dispersant in stabilizing the CNT in water by supplying sufficient repulsive force and minimizing the aggregation effect. Meanwhile, the sonication time, XG concentration and CNT concentration plays a key role in production of stable homogeneous nanofluids. Morphological and thermo-physical properties of CNT nanofluids are measured comprising thermal conductivity and stability behavior.

STABILITY MEASUREMENTS

From Figure 3 is can be seen that the \( R^2 \) value for calibration curve which is defined as a determination coefficient, has a value of >0.95 which indicates a proper fit to the linear regression line. This is indicative of validity and reliability of stability results. Figures 4(a), 4(b), 5(a) and 5(b) demonstrate the effect of XG concentration on stability of CNT suspensions. XG concentration is varied (0.04 and 0.2 wt. %) for each CNT concentration (0.01 and 0.1 wt. %) and the results are plotted for 4.0 h sonication time.

From Figures 4(a), 4(b), 5(a) and 5(b), it is observed that the dispersant added to stabilize the suspension plays a very important role. CNT concentration in the suspension was measured with respect to sediment time to study the sedimentation rate of the nanofluids. Moreover, stabilization of nanofluid required the optimum amount of XG concentration. By increasing the concentration of CNT the respective XG concentration of also increases to adsorb onto the hydrophobic site in order to fully separate the individual tube during sonication. The optimum values of XG concentration were obtained for all the CNT concentrations. The optimum values of CNT and XG concentrations are (0.01 wt. % and 0.1 wt. %) and (0.04 and 0.2 wt. %), respectively. In addition, XG concentration below the optimum value was not adequate in exfoliating the thorough CNT agglomerates and hence caused sedimentation. It should be noted that, the additional amount of dispersant caused in self-aggelomeration and form reverse micelles, therefore cannot adsorbed onto the CNT (Choi et al. 2008; Qi 2006). This study demonstrates that XG dispersant have ability to maintain the dispersion of CNT nanoparticles in the water by overcoming the Van der Waals or attractive forces between the neighboring tubes through steric repulsion. Table 2 shows the optimum XG concentration for each CNT concentration studied.

THERMAL CONDUCTIVITY MEASUREMENTS

Thermal conductivity of the base fluid (water), XG solution and stable CNT nanofluids have been measured at a CNT concentration of 0.01, 0.1 wt. % and XG concentration of 0.04, 0.2 wt. % for temperature ranging from 25 to 70°C is shown in Figures 6 and 7, respectively.

The effect of temperature on CNT-XG nanofluid is investigated with respect to XG and CNT concentration, respectively. Thermal conductivity of water/XG solution is shown in Figure 6. It is observed that by increasing temperature and XG concentration, the thermal conductivity of base fluid decreased. This phenomenon occurs due to the lower thermal conductivity of XG (0.08 * 10^-1 W/mK) compared to the water (6 * 10^-1 W/mK). According to Figure 7, by increasing temperature and CNT concentration, the thermal conductivity of the base fluid increased. This enhancement is more significant for higher CNT concentration (0.1 wt. %) at 50°C. This is due to the Brownian motion of the nanoparticles where the nanoparticles are able to gain more kinetic energy at higher temperature. The CNT with high energy content will tend to move faster and bombard with each other, leading to a substantial increase in the thermal conductivity of nanofluids (Li et al. 2008). As Figures 6 and 7 demonstrated...
FIGURE 4. Effect of xanthan gum (XG) concentration on the stability of CNT: 0.01 wt. % (a) sample images after 800 h of standing at a different XG concentration and (b) CNT concentration vs sediment time.

FIGURE 5. Effect of xanthan gum (XG) concentration on the stability of CNT: 0.1 wt. % (a) sample images after 800 h of standing at a different XG concentration and (b) CNT concentration vs. sediment time.
that CNT have remarkable influence on enhancing thermal conductivity of water compared to XG alone. Rashmi et al. (2011) reported that Brownian motion of nanoparticles at the nanoscale and molecular level is a key mechanism governing thermal behavior of nanofluids, which is also a strong function of temperature. Therefore, it is clear from these figures that dispersant added to stabilize the nanoparticles in suspension does not have a significant role in thermal conductivity enhancement.

### SEM ANALYSIS

The surface morphology of multi walled carbon nanotubes coated with biopolymer xanthan gum was characterized through SEM. Figure 8(a) and 8(b) illustrates the stable nanofluids with low (0.04 wt. %) and high (0.2 wt. %) concentration of biopolymer surfactant, respectively. It can be clearly seen, the surface of nanofluid with low concentration of surfactant was relatively rough which derived from the fact of nanoparticle nature and also incapability of surfactant to provide a good dispersity among nanofluids. As matter of the fact, due to high surface-to-volume of nanoparticles, they have a great capability to interact with their own molecules leading to self-agglomeration phenomena. Moreover, low concentration of surfactant could not cover the entire carbon nanotubes, consequently, rough surface with aggregated nanoparticles observed in Figure 8(a). However, further addition of surfactant not only decreases the self-interaction of nanoparticles but also cover entire nanoparticles; subsequently a smooth surface of nanofluid with good dispersity of nanoparticles illustrated in Figure 8(b). As a result, high concentration of surfactant was adequately ability to settle carbon nanotubes along with xanthan gum, implying the surfactant concentration is directly proportional to stability of nanofluids. It means
that, the increase in surfactant concentration leads to the increase in stability of suspension.

CONCLUSION

This present study investigated the effects of surfactant and nanoparticles concentrations on the stability as well as thermal conductivity of nanofluids. The UV-Vis and K02-Pro methods used to determine the stability and thermal conductivity of suspension nanofluids, respectively. High stability of nanofluids achieved, when the concentration of surfactant increased with the approval of SEM morphology. In nanofluid samples with 0.01 and 0.1 wt. % carbon nanotubes, the optimum concentrations of surfactant were 0.04 and 0.2 wt. %, respectively, to obtain the maximum stability. Whereas, the surfactant concentration influenced on thermal conductivity negligibly since the thermal conductivity of both concentrations were below the water. Interestingly, nanoparticle concentration due to its nature and also temperature raised the thermal conductivity.

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