
Maryam Hosseini,*† Rad Sadri,*†‡ Salim Newaz Kazi,*† Samira Bagheri,‡ Nashrul Zubir,† Chew Bee Teng,† and Tuan Zaharinie†

†Department of Mechanical Engineering, Faculty of Engineering, University of Malaya, Kuala Lumpur 50603, Malaysia
‡Nanotechnology & Catalysis Research Centre (NANOCAT), IPS Building, University of Malaya, 50603 Kuala Lumpur, Malaysia

ABSTRACT: In order to eliminate the use of toxic acids in common carbon nanomaterial functionalization methods, a facile and eco-friendly procedure is introduced in this study to synthesize highly dispersed, covalently functionalized multiwalled carbon nanotubes (MWCNTs) for use in heat transfer fluids. The MWCNTs are treated covalently with clove buds in one pot using a free radical grafting reaction. The clove-treated MWCNTs (C-MWCNTs) are then dispersed in distilled water (DI water) at three different concentrations of C-MWCNTs (0.075, 0.125, and 0.175 wt %), resulting in C-MWCNT-DI water nanofluids. The effectiveness of the functionalization process is then verified using Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), and transmission electron microscopy (TEM). UV–vis spectroscopy is also used to examine the stability of the C-MWCNTs in the base fluid. The thermal conductivity, density, and dynamic viscosity of the C-MWCNT-DI water nanofluids are studied experimentally, and the results show that there is significant thermal conductivity enhancement for the C-MWCNT-DI water nanofluids, whereas there is only a slight increase in the viscosity and density of these nanofluids. Lastly, convective heat transfer experiments are carried out for the C-MWCNT-DI water nanofluids flowing through an annular heat exchanger at constant heat flux and fully developed turbulent flow conditions. The results show that there is a significant enhancement in the convective heat transfer coefficient and Nusselt number for the C-MWCNT-DI water nanofluids, whereas the increase in friction factor is almost negligible for these nanofluids. On the basis of the results, it can be concluded that the eco-friendly C-MWCNT-DI water nanofluids have strong potential for use as effective working fluids in various heat transfer applications.

1. INTRODUCTION

Heating or cooling fluids such as air, water, Freon, ethylene glycol, and mineral oil play a vital role in various industrial sectors such as chemical production, power generation, microelectronics, transportation, and air-conditioning. However, conventional heating or cooling fluids do not have superior capability to transfer or dissipate heat from industrial thermal equipment with high heat flux. One of the promising solutions to address this issue is to disperse nanoparticles with high thermal conductivity (e.g., metal, carbon, or metal oxide nanoparticles) into the base fluid in order to enhance the thermal performance of heat transfer systems. In this regard, Choi et al. found that the thermal conductivity of the CNT-water nanofluids is higher compared to that of water. They measured the effective thermal conductivity of a nanofluid containing 1.0 vol % of multiwalled carbon nanotubes (MWCNTs) dispersed in synthetic poly(α-olefin) oil and reported a thermal conductivity enhancement of 160%. Sadri et al. studied the sonication time effect on the dynamic viscosity, thermal conductivity, and dispersion of MWCNT aqueous suspensions. The results represented that the viscosity decreases, whereas the thermal conductivity of the nanofluids increases with an increase in temperature and sonication time. The maximum thermal conductivity enhancement was found to be 22.31% (ratio of 1.22) at a temperature and sonication time of 45 °C and 40 min, respectively. Philip et al. investigated the thermal conductivity enhancement of kerosene-based Fe₃O₄ nanofluids under the influence of a magnetic field and the results showed that the enhancement of thermal conductivity is 300% ($k_{\text{nanofluid}}/k_{\text{base fluid}} = 4.0$) at a concentration of 6.3 vol % and particle size of 6.7 nm. Pak and Cho investigated the heat transfer performance of γ-Al₂O₃ and TiO₂ nanoparticles dispersed in water flowing through a horizontal circular tube under turbulent flow and constant heat flux conditions. The results represented that the Nusselt number of the nanoparticles aqueous suspensions increases by increasing the Reynolds number and nanoparticle concentration. Moreover, they discovered that the convective heat transfer coefficient of the nanofluids is lower than that for water by 12% for a given condition when the particle loading is 3 vol %. They proposed a new heat transfer correlation to predict the convective heat transfer coefficient of nanofluids in a turbulent flow regime. Annular heat exchangers are commonly used in industrial applications, particularly in heat transfer equipment. These heat exchangers have gained much attention from scientists and researchers, and they have been used in various...
thermal systems such as air-conditioning, electronic devices, heating and ventilation systems, turbomachinery, gas turbines, and nuclear reactors. Hence, investigating the heat transfer characteristics of annular heat exchangers and devising a novel technique to improve their performance play a key role in promoting energy savings.2,15 Weerapun Duangthongsuk et al.14 studied the friction factor and convective heat transfer of TiO$_2$ aqueous suspensions (concentration of 0.2 vol %) in a horizontal double-tube counter flow heat exchanger under turbulent conditions. They discovered that the convective heat transfer coefficient of nanofluids is slightly greater than that of the base fluid by about 6−11% and increases by decreasing the fluid temperature. Moreover, they showed that the temperature of the heating fluid has no significant effect on the heat transfer coefficient of the nanofluid. Izadi et al.15 simulated the forced convection flow of Al$_2$O$_3$/water aqueous suspensions through a two-dimensional annular heat exchanger (in which the working fluid was Al$_2$O$_3$-water nanofluid) using the single-phase method under turbulent conditions. The results showed that the dimensionless axial velocity profile does not remarkably vary with the nanoparticle volume fraction. However, the temperature profiles are affected by the nanoparticle concentration. They found that the convective heat transfer coefficient increases by increasing the nanoparticle concentration. CNTs have garnered much interest among scientists and researchers because of their remarkable physical and chemical properties16,17 as well as excellent mechanical properties.18−20 Indeed, it has been proven in previous studies that CNT nanofluids have high thermal and electrical conductivities.21−24 However, the main disadvantage of CNTs is their poor solubility and processability since they easily become entangled, and moreover, they tend to aggregate in most organic and aqueous solvents.25 It has been shown that noncovalent functionalization of CNTs based on the π−π stacking interaction and polymer wrapping of surfactants such as sodium dodecyl benzene sulfonate (SDBS), sodium dodecyl sulfate (SDS), gum arabic (GA), and cetyltrimethylammonium bromide (CTAB) improves the solubility of CNTs in polar solvents.9,18,26 However, there are some undesirable effects of the above-mentioned surfactants on the thermophysical properties of carbon based nanofluids such as increasing viscosity and foam formation in the colloidal suspensions which have limited surfactant applications.27 On the other hand, various techniques have been employed for covalent modification of carbon nanotubes such as treatment with ozone, oxidation, fluorination, free radical addition, 1,3-dipolar cycloaddition, nucleophilic addition, alkylation, and plasma modification.28−30 Among these techniques, free radical grafting is a desirable technique for large-scale synthesis of CNTs with versatile functional groups due to its facile treatment and high reactivity.21 In this technique, peroxides, aryldiazonium salts, substituted anilines, or benzophenone are used as the starting materials.28,30 However, all of the aforementioned techniques typically require very harsh and drastic reaction conditions. In addition, most of these techniques involve many reaction steps, and the reagents and chemicals employed in these techniques are greatly prone to oxidation. These techniques can also damage the sp$^3$ hybridized carbon atoms of nanotubes, which in turn, have an effect on the thermal, electrical, and optical properties of the carbon nanotubes.28 These techniques also lead to other problems such as health hazards, equipment corrosion, and environmental pollution. Hence, there is a critical need to develop a functionalization method which is environmentally friendly31 in order to tackle the above-mentioned issues. Clove, an aromatic flower bud, is one of the most widely cultivated spices in tropical countries. Clove bud is one of the main vegetal sources of phenolic compounds such as hydroxybenzoic acids, flavonoids, hydroxycinnamic acids, and hydroxypHENYL propane.32 Eugenol is the major bioactive compound of cloves, which is typically found in concentrations of around 82.6 wt %.33 Phenolic acid and gallic acid are also present in cloves at higher concentrations. A previous study34 has shown that ascorbic acid is found in clove flower buds with concentrations up to 0.08 wt %. The unique properties and structure of cloves make them a suitable candidate to improve the functionalization of CNTs in aqueous media. Hence, the main objective of this study is to develop an environmentally friendly, cost-effective, and industrially scalable method for synthesizing MWCNTs covalently functionalized with cloves and to determine the effectiveness of this technique in improving convective heat transfer in an annular heat exchanger relative to that for water. In order to verify the success of the functionalization method, the clove-treated MWCNTs are characterized using Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), transmission electron microscopy (TEM), and ultraviolet−visible (UV−vis) spectroscopy. Following this, the clove-treated MWCNTs are dispersed into distilled water at three different nanoparticle concentrations (0.075, 0.125, and 0.175 wt %) to prepare C-MWCNT-DI water nanofluids and the rheological and thermo-physical properties of these nanofluids also investigated at various temperatures. The friction factor and Nusselt number values for the base fluid are determined from the experimental data, and the results are validated against those calculated from empirical correlations. Lastly, the Nusselt number, convective heat transfer coefficient, pressure drop, friction factor, and performance index are evaluated for the C-MWCNT-DI water nanofluids flowing through an annular heat exchanger in turbulent flow conditions.

2. MATERIALS AND METHODS

Pristine multiwalled carbon nanotubes (MWCNTs) with a diameter less than 30 nm and a purity of more than 95% were purchased from Nanostructured & Amorphous Materials Inc. (Houston, TX, USA). Hydrogen peroxide (H$_2$O$_2$, 30%) was purchased from Sigma-Aldrich (M) Sdn. Bhd., Selangor, Malaysia. Fresh cloves, which are a source of eugenol and vitamin C (ascorbic acid), were purchased from a grocery store in Iran.2.1. Preparation of C-MWCNT-DI Water Nanofluids. A novel, facile, and eco-friendly technique for covalent functionalization of MWCNTs with cloves by employing free radical grafting method was introduced for the first time in this study in order to attain highly dispersed MWCNTs in aqueous media. In this technique, eugenol (which is the main component of cloves35) was grafted onto the MWCNTs using hydrogen peroxide and ascorbic acid (also a component of cloves) as the redox initiator.34 In this method, ascorbic acid reacts with hydrogen peroxide (a free-radical oxidizer that generates non-toxic by-products and leaves no chemical residue), producing hydroxyl radicals. Also at high temperatures, the hydrogen peroxide becomes unstable and decomposes spontaneously into hydroxyl radicals. The generated hydroxyl radicals will attack eugenol and produce free radicals on their structure, which leads to linkage of the activated eugenol onto the surface of MWCNTs. The clove extract solution was prepared using the following procedure. First, 20 g of ground cloves were added into a beaker containing 1000 mL of distilled water and preheated at 80 °C. The solution was then homogenized in heating mode at an agitation speed of 1000 rpm for
Lastly, the clove extract solution was filtered using a 45 μm polytetrafluoroethylene (PTFE) membrane in ambient conditions.

The clove-treated MWCNTs (C-MWCNTs) were prepared using the following procedure. First, 5 g of pristine MWCNTs were poured into a beaker filled with 1000 mL of clove extract solution, followed by continuous stirring for 15 min in order to achieve a uniform black suspension. Following this, 35 mL of concentrated hydrogen peroxide was added gradually into the reaction mixture throughout the sonication time. The reaction mixture was ultrasonicated for 10 min. After sonication, the reaction mixture was heated to 80 °C under reflux for 14 h. The resultant suspension was centrifuged repeatedly at 14000 rpm and then washed with large amounts of distilled water until the suspension attained a neutral pH. The functionalized sample was dried overnight in a vacuum oven set at 60 °C. It was observed that the clove-treated MWCNTs are highly stable in aqueous medium.

In order to synthesize the C-MWCNT-DI water nanofluids, the C-MWCNTs were ultrasonicated with distilled (DI) water as the base fluid for 10 min. The nanofluids were prepared for three different concentrations of C-MWCNTs: 0.075, 0.125, and 0.175 wt %. The sample preparation procedure is summarized in Figure 1.

2.2. Experimental Procedure. The experiments were carried out in several stages. First, the pristine MWCNTs were covalently functionalized with cloves, and the C-MWCNTs were characterized using various analytical instruments. Following this, the thermophysical properties of the synthesized nanofluids and base fluid were determined. Lastly, the convective heat transfer and frictional properties of the C-MWCNT-DI water nanofluids flowing through an annular heat exchanger were investigated. Characterization of the C-MWCNTs was carried out using Fourier transform infrared (FTIR) spectroscopy (Bruker, IFS-66/S, Germany) and thermogravimetric analysis (TGA-50, Shimadzu, Japan). Hitachi HT7700 transmission electron microscope was used to examine the morphological characteristics of the samples. For the TEM analysis, the samples were prepared by ultrasonically dispersing the nanoparticles in ethanol prior to collection on Lacey carbon grids. We used a Shimadzu UV-1800 spectrophotometer to determine the dispersibility of C-MWCNT-DI water nanofluids. For the UV–vis analysis, we diluted the nanofluids with DI water at a dilution ratio of 1:20 in order to ensure that the detectable wavelengths of the UV–vis spectrometer are able to pass through the samples. Following this, we poured our samples into quartz cuvettes specialized for the transmission of UV wavelengths, and we measured the absorbance of the samples at predefined time intervals over the course of 63 days. The thermal conductivity of the samples was measured using a KD-2 PRO portable field and laboratory thermal property analyzer (Decagon Devices, USA). The KS-1 probe has a length and diameter of 60 and 1.3 mm, respectively. The accuracy of the thermal conductivity measurements is around 5%. In order to ensure equilibrium of the nanofluids, an average of 20 measurements were recorded over a 5-h period for each nanoparticle concentration and temperature. Calibration of the instrument was also conducted with DI water prior to measurements using nanofluids. The viscosity of the nanofluids was measured using a Physica MCR rheometer (Anton Paar, Austria). The rotational rheometer consists of a moving cylindrical plate and a stationary cylindrical surface placed in parallel with a small gap between them. The density of the samples was measured using a DE-40 density meter (Mettler Toledo, Switzerland), with an accuracy of 10⁻⁴ g/cm³. The measurements were made in triplicate for each sample and temperature. The overall experimental setup for convective heat transfer measurements includes an annular flow test rig, a reservoir tank, a pump, a data acquisition system, a cooling unit, a heated test section, and measuring instruments including a differential pressure transmitter (DPT) and a flow meter. The experimental setup is shown in Figure 2.
in Figure 2. The aqueous suspensions were pumped using an Araki EX-70 R magnet pump from a 10 L stainless steel jacketed tank at a flow rate of $0\sim14$ L/min. The pressure loss and flow rate were measured using PX154 wet/wet low differential pressure transmitter (OMEGA Engineering Inc., USA) and an SE 32 inline paddle wheel transmitter with display (Bürkert Contromatic Corp., USA), respectively. The pump flow was regulated using a Hořman Muller inverter. The concentric annular test rig consists of a cartridge heater (OMEGA Engineering Inc., USA) with a length of 600 mm and a diameter of 15 mm, which was inserted in the center of a straight, seamless, and horizontal tube made from stainless steel with a length of 900 mm and outer and inner diameters of 33.4 and 26.7 mm, respectively. The heater was linked to a QPS VT2-1 variable voltage transformer (Success Electronics & Transformer Manufacturer Sdn. Bhd., Malaysia), and voltage and current were measured to set the desired heating power. Three built-in K-type thermocouples (OMEGA Engineering Inc., USA) were cautiously installed a little away from the outside contact face of heater surface in order to prevent disturbance in the boundary layer caused by the thermocouple probes protruding into the internal surface of the tube. The bulk temperature of the flow was measured using two platinum resistance temperature detectors (Pt-100 RTDs) which were placed inside the pipe at the outlet and inlet of the test section. The maximum error for thermocouples was $\pm0.2^\circ C$. The heat flux was determined using the following equation:

$$ q^* = \frac{Q}{A} $$

Here, $Q$ is the input power (VI) generated by the voltage transformer, and $A$ is the internal surface area of the tube. Note that $A = \pi D_h L$. $D_h$ is the annulus hydraulic diameter, which is defined as the difference between the inner tube diameter and outer heater diameter. $L$ is the annulus heated length. The input power (VI) was kept fixed at 900 W for the experiments. The Reynolds number ($Re$) was calculated using the following equation:

$$ Re = \frac{\rho v D_h}{\mu} $$

where $\rho$, $v$, and $\mu$ represents the density, velocity, and dynamic viscosity of the working fluid, respectively. The Nusselt number is given by

$$ Nu = \frac{h \times D_h}{k} $$

where $k$ and $h$ represent the thermal conductivity and convective heat transfer coefficient, respectively. The friction factor ($f$) of the DI water and C-MWCNT-DI water nanofluids was determined from the pressure drop across the test section measured from experiments using the following eq (eq 5):

$$ f = \frac{\Delta P}{\frac{1}{2} \rho v^2 L} $$

Figure 3. (A) FTIR spectra of pristine MWCNTs and C-MWCNTs, (B) TGA curves of pristine MWCNTs and C-MWCNTs, and (C) photograph of C-MWCNTs dispersed in DI water after three months.
Where, $\Delta P$ and $\nu$ represent the pressure drop and flow velocity, respectively.

### 3. RESULTS AND DISCUSSION

#### 3.1. Characterization of the C-MWCNTs

In this study, various characterization techniques were used to characterize the C-MWCNTs. The morphology of the C-MWCNTs was examined using TEM. FTIR spectroscopy was used to identify the functional groups attached to the C-MWCNTs. Figure 3A shows the FTIR spectra for the pristine MWCNTs and C-MWCNTs, which are represented by the transmittance (%) versus the wavenumber (cm$^{-1}$). It can be observed from Figure 3A that there are noticeable cues of the eugenol molecule for the C-MWCNTs compared to the pristine MWCNTs. The broad peak at 3448.19 cm$^{-1}$ is ascribed to O–H stretching vibrations, which may be caused by the reaction between the MWCNTs and hydroxyl groups of eugenol and/or hydrogen peroxide. The symmetric and asymmetric sharp vibrations of C–H bonds are observed within a wavenumber range of 2850–3000 cm$^{-1}$ for both MWCNTs and C-MWCNTs. A couple of peaks are observed within the wavenumber range of 1579–1639 cm$^{-1}$, which arise from C=C stretching vibrations of MWCNTs after opening due to the addition of electrophilic reactions between the main structure of MWCNTs and the OH band of eugenol. The functionalization of MWCNTs by eugenol is confirmed by the peaks at 1428, 1386, and 1077–1113 cm$^{-1}$, which are ascribed to CH$_2$ bending vibrations, out-of-plane CH vibrations, and C–O stretching vibrations, respectively. The peaks within the wavenumber range of 1722–1763 cm$^{-1}$ and the peak centered at 1621 cm$^{-1}$ are assigned to O–C=O stretching vibrations, indicating the formation of carboxyl groups at the main structure of MWCNTs.

TGA is a thermal analysis technique, whereby modifications in the structure of materials are evaluated as a function of temperature. TGA provides information about the quantitative amount of each functional group on the surface of MWCNTs, which is why it was used to characterize the pristine MWCNTs and C-MWCNTs. Figure 3B shows the TGA curves for pristine MWCNTs and C-MWCNTs, and it can be seen that there is no weight loss in the pristine MWCNTs up to a temperature of $\sim$700 °C, which is the temperature at which the main graphitic structures begin to decompose. However, there is a gradual weight loss for the C-MWCNTs, which confirms the decomposition of the functional groups. There are three distinctive steps of weight loss for the clove-treated MWCNTs within a temperature range of 0–600 °C. The first weight loss occurs at $\sim$100 °C, which is attributed to water, whereas the second weight loss occurs between 200 and 300 °C, which is due to the decomposition of the functional group (i.e., eugenol). The third weight loss occurs after 600 °C, which is caused by the degradation of the graphitic structures in air. The results indicate the successful covalent functionalization of MWCNTs with eugenol, which is evidenced by the gradual weight loss observed in the TGA curve for C-MWCNTs. A digital image of C-MWCNTs dispersed in DI water after 90 days is shown in Figure 3C.

Even though the functional groups cannot be inferred from TEM images, these images can be used to examine the surface deterioration of MWCNTs, as evidence of functionalization. Figure 4A–C shows the TEM images of pristine MWCNTs and C-MWCNTs. It can be observed that the pristine MWCNTs have a relatively smooth surface and low wall roughness for the modified MWCNTs within a temperature range of 0–600 °C. The first weight loss occurs at $\sim$100 °C, which is attributed to water, whereas the second weight loss occurs between 200 and 300 °C, which is due to the decomposition of the functional group (i.e., eugenol). The third weight loss occurs after 600 °C, which is caused by the degradation of the graphitic structures in air. The results indicate the successful covalent functionalization of MWCNTs with eugenol, which is evidenced by the gradual weight loss observed in the TGA curve for C-MWCNTs. A digital image of C-MWCNTs dispersed in DI water after 90 days is shown in Figure 3C.

Even though the functional groups cannot be inferred from TEM images, these images can be used to examine the surface deterioration of MWCNTs, as evidence of functionalization. Figure 4A–C shows the TEM images of pristine MWCNTs and C-MWCNTs. It can be observed that the pristine MWCNTs have a relatively smooth surface and low wall roughness for the modified MWCNTs within a temperature range of 0–600 °C. The first weight loss occurs at $\sim$100 °C, which is attributed to water, whereas the second weight loss occurs between 200 and 300 °C, which is due to the decomposition of the functional group (i.e., eugenol). The third weight loss occurs after 600 °C, which is caused by the degradation of the graphitic structures in air. The results indicate the successful covalent functionalization of MWCNTs with eugenol, which is evidenced by the gradual weight loss observed in the TGA curve for C-MWCNTs. A digital image of C-MWCNTs dispersed in DI water after 90 days is shown in Figure 3C.

Figure 4. TEM images of (A) pristine MWCNTs and (B and C) C-MWCNTs.

DI water nanoﬂuids with respect to the number of days after preparation. It is obvious that the relative concentration of the aqueous suspensions reduces with the number of days. However, all of the samples have a fairly constant concentration after day 45. The maximum magnitude of sedimentation is 7.6, 9.2, and 11.3% for a nanoparticle concentration of 0.075, 0.125, and 0.175 wt %, which confirms the colloidal stability of the nanoﬂuids containing C-MWCNTs.

#### 3.2. Thermophysical Properties

The effective viscosity of nanoﬂuids containing C-MWCNTs and DI water were measured experimentally, and the results are shown in Figure 6. The dynamic viscosity is shown as a function of the nanoparticle concentration and temperature at a fixed shear rate of 150 s$^{-1}$. It can be observed that there is a slight increase in
the dynamic viscosity of the C-MWCNT-DI water nanofluids relative to that for DI water. This indicates that the C-MWCNTs remain suspended in the base fluid, which indicates successful covalent functionalization. It can also be observed from Figure 6 that the dynamic viscosity of the C-MWCNTs nanofluids declines by increasing temperature, which may be attributed to the weakening of intermolecular forces. This observation corroborates well the findings of Aravind et al., Ko et al., and Sadri et al., who observed that there is decrease in viscosity when the fluid temperature is increased. The rather mild increase in the effective viscosity with nanoparticle concentration is an important advantage since the increase in viscosity could undermine the overall positive impact of enhanced conductivity in heat transfer due to the pumping fluid penalty.

The density was measured for the C-MWCNT aqueous suspensions and base fluid at various temperatures, and the results are presented in Table 1. It can be seen that there is a decrease in the density of the C-MWCNT-DI water nanofluids and DI water with an increase in fluid temperature, which can be attributed to the liquid thermal expansion. There is a slight increment in the density for the C-MWCNT-DI water nanofluids with an increase in nanoparticle concentration. The increase in density can be attributed to the density of the C-MWCNTs, which is higher than that of the base fluid. Hence, increasing the particle loading will increase the density of the nanofluid. The maximum increase in density of the C-MWCNT-DI water nanofluid is 0.08% for a nanoparticle concentration of 0.175 wt % at 20 °C. However, the density decreases by approximately 0.6% when the temperature is increased from 20 to 40 °C for the same nanoparticle concentration.

The thermal conductivity of a coolant is one of the parameters that play a significant role in increasing the heat transfer rate of heat exchangers. Hence, the thermal conductivity of the C-MWCNT-DI aqueous suspensions was measured experimentally in this study, and the results are shown in Figure 7. The thermal conductivity of the C-MWCNT-DI water nanofluids was plotted as a function of temperature and nanoparticle concentration. It should be noted that only nanofluids with low concentrations of C-MWCNTs were considered in this study in order to prevent a drastic increase in viscosity. The thermal conductivity of the base fluid was compared with that from the National Institute of Standards and Technology (NIST) database, and there is good agreement between these values, whereby the error is less than 1%. It is evident from Figure 7 that the thermal conductivity of the C-MWCNT-DI water nanofluids is significantly greater than that for the base fluid. Moreover, it is evident that the thermal conductivity of the C-MWCNT aqueous suspensions and base fluid increases with an increase in fluid temperature. Nonetheless, the thermal conductivity enhancement is higher for the C-MWCNT-DI water nanofluids at higher nanoparticle concentrations. On the basis of Figure 7, it can be deduced that temperature plays a vital role in enhancing the effective thermal conductivity of nanofluids, which is due to the Brownian motion of the C-MWCNTs dispersed in the base fluid. The maximum thermal conductivity enhancement obtained is 20.15% for a nanoparticle concentration of 0.175 wt % at 50 °C.

The empirical correlation proposed by Petukhov and Gnielinski for the turbulent flow regime. These empirical correlations are given by eqs 6 and (7), respectively.

\[
Nu = \frac{\left(\frac{f}{8}\right) Re Pr}{1.07 + 12.7 \left(\frac{f}{8}\right)^{0.3} (Pr^{2/3} - 1)}
\]

where

- \(Nu\) is the Nusselt number
- \(Re\) is the Reynolds number
- \(Pr\) is the Prandtl number
- \(f\) is the friction factor
- \(\frac{f}{8}\) is the Darcy friction factor

The heat transfer rate of heat exchangers. Hence, the thermal conductivity of the C-MWCNT-DI water nanofluids was measured experimentally in this study, and the results are shown in Figure 7. The thermal conductivity of the C-

![Figure 6. Dynamic viscosity of nanofluids containing C-MWCNTs and DI water at a shear rate of 150 s⁻¹ (mPa·s).](image)

![Figure 7. Thermal conductivity of C-MWCNT-DI water nanofluids and DI water.](image)
where the friction factor \( f \) is defined as, \( f = (0.79 \ln \text{Re} - 1.64)^{-2} \).

It should be noted that eq 6 is applicable for a Reynolds number range of \( 4000 < \text{Re} < 5 \times 10^8 \) and Prandtl number range of \( 0.5 < \text{Pr} < 2000 \).

\[
\text{Nu} = \frac{(f_{\text{ann}}/8)\text{RePr}}{k_1 + 12.7\sqrt{f_{\text{ann}}/8(\text{Pr}^{2/3} - 1)}} \left[ 1 + \left(\frac{D_h}{L}\right)^{2/3} \right] F_{\text{ann}} K
\]

(7)

with

\[
k_1 = 1.07 + \frac{900}{\text{Re}} - \frac{0.63}{(1 + 10\text{Pr})}
\]

(8)

Eq 7 is used for a Reynolds number range of \( \text{Re} > 4000 \), a Prandtl number range of \( 0.1 < \text{Pr} < 2000 \), and the factor \( F_{\text{ann}} \) in eq 7 representing the boundary condition of heat transfer at the inner wall with the outer wall insulated and the factor \( K \) for liquids as variation of fluid properties with temperature can be calculated by eqs 9 and 10, respectively.

\[
f_{\text{ann}} = 0.75a^{-0.17}
\]

(9)

\[
K = \left(\frac{\text{Pr}_b}{\text{Pr}_w}\right)^{0.11}
\]

(10)

The friction factor \( f_{\text{ann}} \) in eq 7 is given by Gnielinski\(^4\) as

\[
f_{\text{ann}} = (1.8 \log \text{Re}^* - 1.5)^{-2}
\]

(11)

where

\[
\text{Re}^* = \text{Re} \left(\frac{1 + a^2}{(1 - a)^2}\ln a + \frac{1 - a^2}{(1 - a)^2}\ln a\right)
\]

(12)

Figure 8 shows the comparison between the experimentally measured average Nusselt number and those calculated using the aforementioned empirical correlations for the base fluid at a fixed water inlet temperature of 30 °C. Indeed, the Nusselt number increases with an increase in the Reynolds number, as expected. The maximum error between the values obtained from experiments and Petukhov\(^3\) and Gnielinski\(^4\) empirical correlation is found to be approximately 3.5 and 9.5%, respectively. In general, the results obtained from the experiments are in good agreement with those from empirical correlations within the range of the Reynolds number investigated in this study. Hence, it can be deduced that the experimental setup is reliable and that it can be utilized to assess the heat transfer properties of the C-MWCNT aqueous suspensions.

A series of experiments were conducted for the C-MWCNT-DI water nanofluids (nanoparticle concentration: 0.075, 0.125, and 0.175 wt %) by varying the Reynolds number from 3055 ±5 to 7944 ±5 in order to determine the convective heat transfer of the aqueous suspensions in turbulent flow regime. The input power was kept fixed at 900 W. The results are shown in Figure 9 for a constant inlet temperature of 30 °C. It can be observed that the convective heat transfer coefficient increases when the Reynolds number is increased for both the base fluid and C-MWCNT-DI water nanofluids. It can also be observed that the nanoparticle concentration affects the heat transfer coefficient of the nanofluids. The remarkable enhancement in convective heat transfer coefficient of the C-MWCNT-DI water nanofluids is mainly due to the narrow thermal boundary layer resulting from the thermal conductivity enhancement of C-MWCNT-DI water nanofluids as well as a decrease in thermal resistance between the flowing nanofluids and inner wall surface of the annular tube at higher Reynolds numbers. According to refs 1 and 36, carbon nanomaterials (e.g., carbon nanotubes and graphene nanoplatelets) tend to reduce the thickness of the thermal boundary layer. The specific surface area and Brownian motion of the nanoparticles also play a role in influencing the convective heat transfer coefficient. In this study, the convective heat transfer coefficient of the nanofluids increases by 12.38, 24.1, and 35.89% for a nanoparticle concentrations of 0.075, 0.125, and 0.175 wt %, respectively.

Figure 9. Variation of the average heat transfer coefficient for C-MWCNT/DI water nanofluids versus the Reynolds number.

To assess the convective-to-conductive heat transfer ratio of C-MWCNT aqueous suspensions, the average Nusselt number determined from eq 4 was plotted as a function of Reynolds number and nanoparticle concentration. The results are shown in Figure 10, and it can be seen that there is a significant increase in the Nusselt number with an increase in the Reynolds number as well as the concentration of C-MWCNTs relative to that for the base fluid. The greater Nusselt number for the C-MWCNT nanofluids is attributed to the higher thermal conductivity of the nanofluids, which is associated with the Brownian motion of the C-MWCNTs.\(^4\) The maximum

Figure 8. Comparison between the measured Nusselt numbers of DI water with those calculated from empirical correlations.
Reynolds number is shown in Figure 12A. The corresponding friction factor values were calculated using eq 5, and the results setup used to measure the pressure drop is validated for the less than 4.15%. Hence, it can be stated that the experimental experiments and those calculated using the Gnielinski empirical correlation is only a slight deviation between the data obtained from experiments and empirical correlation.

In order to validate the pressure drop accuracy in the experimental setup, the variation of the measured friction factor for the DI water was compared with the values calculated from empirical correlation proposed by Gnielinski (eq 11), and the results are shown in Figure 11. It can be observed that there is only a slight deviation between the data obtained from experiments and those calculated from empirical model. The deviation between the experimental friction factor values and those calculated using the Gnielinski empirical correlation is less than 4.15%. Hence, it can be stated that the experimental setup used to measure the pressure drop is validated for the range of Reynolds number investigated in this study.

The pressure drop of the C-MWCNT-DI water nanofluids flowing through the test section recorded over a range of Reynolds number is shown in Figure 12A. The corresponding friction factor values were calculated using eq 5, and the results are shown in Figure 12B. The results show that there is a small increment in both the pressure drop and friction factor for the C-MWCNT-DI water nanofluids relative to those for DI water. The maximum increase in the friction factor and pressure drop is found to be ~3% and 23%, respectively, for a nanoparticle concentration of 0.175 wt %. This increment in pressure drop is mainly due to the slight increment in viscosity for all C-MWCNT-DI water nanofluids (Figure 6) which required a slight increment in fluid velocity since the corresponding Reynolds number is constant (eq 3). Hence, it can be seen that the velocity of the working fluid plays a vital pattern in increasing the pressure drop and friction factor compared to that of DI water in convective heat transfer systems. This matter can be acknowledged by revisiting eq 5 for the pressure drop and friction factor, and eq 3 for the Reynolds number.

The performance index ($\varepsilon$) was calculated using eq 13 in order to assess the economic performance of the novel, eco-friendly C-MWCNT-DI water nanofluids synthesized in this study as potential fluids in heat transfer systems such as solar collectors and heat exchangers.

$$\varepsilon = \frac{h_{\text{eff}}}{h_{\text{f}} \Delta \rho_{\text{eff}} / \Delta \rho_{\text{f}}} = \frac{R_{\text{f}}}{R_{\text{dp}}}$$

where $R_{\text{dp}}$ is the ratio of pressure drop of the C-MWCNTs aqueous suspensions to the base fluid, and $R_f$ is the ratio of heat transfer enhancement of C-MWCNTs nanofluids relative to the base fluid. Figure 13 indicates the performance index of the C-MWCNT aqueous suspensions over a range of Reynolds number and various nanoparticle concentrations. It can be observed that the performance index is higher than 1 for all samples, which shows the advantage of using these novel nanofluids in heat transfer systems. It is apparent that the performance index increases with increasing the concentration of C-MWCNTs in the base fluid. This implies that these eco-friendly nanofluids have higher effectiveness when the particle loading is increased. Figure 13 shows that the performance index of the C-MWCNT nanofluids tends to increase with an increase in the Reynolds number (regardless of the nanoparticle concentration), indicating that the C-MWCNT-DI water nanofluids are suitable alternative coolants for heat transfer applications.

4. CONCLUSION

An environmentally friendly and cost-effective procedure for synthesizing covalently functionalized multiwalled carbon nanotubes with cloves (C-MWCNTs) has been developed in this study. The C-MWCNT-DI water nanofluids are then prepared by ultrasonication C-MWCNTs with distilled water as the base fluid for three different nanoparticle concentrations (i.e., 0.075, 0.125, and 0.175 wt %). The potential of these nanofluids as heat transfer fluids is investigated by convective heat transfer experiments through an annular heat exchanger at a turbulent flow regime. The exceptional performance of the functionalization method is confirmed by TGA, FTIR spectroscopy, UV–vis spectroscopy, and TEM. On the basis of the UV–vis absorption spectra, the C-MWCNT-DI water nanofluids have remarkable stability over the course of 63 days. On the basis of the thermo-physical properties of the C-MWCNT-DI water nanofluids, it can be deduced that these nanofluids are potential working fluids in heat transfer systems. It is found that there is significant enhancement in the convective heat transfer coefficient and Nusselt number up to 35.89 and 20.15%, respectively. This significant enhancement is attained at a Reynolds number of 7944, nanoparticle concentration of 0.175 wt %, and constant heat flux of 38346 W/m². The maximum increase in friction factor of the C-MWCNT-DI water

![Figure 10](image-url) Variation of the Nusselt number for C-MWCNT-DI water nanofluids as a function of the Reynolds number.

![Figure 11](image-url) Plot of the friction factor as a function of Reynolds number for DI water obtained from experiments and empirical correlation.

![Figure 12](image-url) Graph showing the variation of the friction factor and pressure drop for different Reynolds numbers.
nano fluids is about 3%, relative to that for the base fluid, for a nanoparticle concentration of 0.175 wt %. In addition, it was found that the performance index of the C-MWCNT-DI water nano fluids is more than 1 (regardless of the nanoparticle concentration investigated in this study), indicating that these nano fluids are potential working fluids in heat transfer systems in terms of overall thermal performance and energy savings.

■ AUTHOR INFORMATION

Corresponding Authors
*(M.H.) Tel: +60 3 79674582. Fax: +60 3 79675317. E-mail: hoseini.sma@gmail.com.
*(R.S.) E-mail: rod.sadri@gmail.com.
*(S.N.K.) E-mail: salimnewaz@um.edu.my.

ORCID

Rad Sadri: 0000-0002-8260-7994

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge the financial support provided by University of Malaya under the Fundamental Research Grant Scheme (Project no. FP060-2015A) and University of Malaya Research Grant Scheme (project no. RP012B-13AET). We also greatly appreciate the assistance provided by the technical and administrative staff of the Faculty of Engineering, University of Malaya, in carrying out this study.

■ REFERENCES

(14) Duangthongtuk, W.; Wongswises, S. Heat transfer enhancement and pressure drop characteristics of TiO 2–water nano fluid in a


