Thermal Conductivity and Viscosity of Bio-based Carbon Nanotubes: Review

Gloria A. Adewumi*‡, Andrew Eloka-Eboka**, Freddie Inambao***

*Discipline of Mechanical Engineering, School of Engineering, PhD candidate, Room 138B, Discipline of Mechanical Engineering, University of KwaZulu-Natal, Howard College

** Discipline of Mechanical Engineering, School of Engineering, Post-doctoral Fellow, Green Energy Solutions, Discipline of Mechanical Engineering, University of KwaZulu-Natal, Howard College

*** Discipline of Mechanical Engineering, School of Engineering, Professor, Discipline of Mechanical Engineering University of KwaZulu-Natal, Howard College

(adewumigloria@gmail.com, fatherfounder@yahoo.com, inambaof@ukzn.ac.za)

‡ Corresponding Author; Gloria Adewumi, Room 138B Discipline of Mechanical Engineering, University of KwaZulu Natal, Durban, South Africa, Tel: +27749423154, adewumigloria@gmail.com

Received: 10.04.2017 Accepted:16.07.2017

Abstract- Significant research focus is being channeled to carbon nanotubes (CNTs) obtained from biomass precursors because of their overall environmental acceptability, stability, low toxicity and simplistic use. They contain unique properties such as high viscosity, high aspect ratio, special surface area and high thermal conductivity which have been identified to be responsible for their improved heat transfer applications. High thermal conductivity of this class of nanomaterials is linked to the presence of phonons. Thus, knowledge of the principle of heat conductivity in carbon nanotubes encompasses investigations relating to the dissimilarity in the different phonon modes. Also, an in-depth understanding in which phonon modes play the governing role is necessary. Herein the authors have carried out a critical review of past and current literature, the function of phonon relaxation rate primarily governed by three-phonon Umklapp scattering process and boundary scattering have been explored. Also the roles of temperature and shearing time on viscosity of CNT fluids are discussed. Results indicate that the sensitivity of the phonon modes is due to several nanotube parameters like: temperature, diameter, axial strain, defects and length. The various viscosity experiments from literature shows that the kinematics viscosity of nanofluids improved with a decrease in the temperature and increase of the CNT concentration.

Keywords- Bio-based carbon nanotubes, Phonons, Thermal conductivity, Umklapp process, Viscosity.

1. Introduction

A “biomaterial” or a “bio-based material” is produced from existing living organisms including residues and agricultural crops, algae and trees. “Sustainable bio-based materials” are materials obtained from mature and reaped cropland or plantations which are sustainable; synthetized without harmful contributions and influences; are harmless and healthy for the environment during usage [1-5], and are intended to be reused at the end of their proposed use via composting and recycling.

Due to their unique mechanical, electrical and thermal properties, a growing effort is being made to deviate from the heavy dependence on petroleum sources for energy. Bio-materials obtained from green sources pose no health hazards and is friendlier on ozone depletion. Past study has suggested a focus towards the formation of value added materials obtained from bio-mass instead of using biomass as a direct source of fuel [6-10].

In 1991 after their discovery, research on Carbon Nanotube (CNTs) has emerged, branching open new discoveries and opportunities. CNTs have wonderful heat and electrical transfer properties which makes them a sort of wonder material. The diversity in property which is an advantage stems from their abilities to be rolled up in different tube axis based on different helicities [11] and this is decided by a chiral vector which categorizes CNTs into “zigzag", "armchair”, and “chiral” forms. Carbon nanotubes are one-dimensional cylinders and can be multiple or single layers of carbon. Nanotubes with a one layer are called Single Wall Carbon Nanotubes (SWCNTs) while carbon nanotubes with multiple walls are called Multi-wall Carbon Nanotubes (MWCNTs) [12]. The diameters of the tubes are in the range of a few nanometers (0.4nm-1.4nm) and a length in micrometers, which confers high aspect ratios [11]. MWCNTs are easier to synthesize when compared to SWCNT because they can be grown from most hydrocarbons at a low temperature (600-900^{o}C). SWCNTs are usually synthesized by infusing metals in the transition metals group in catalytic amounts in the arc-discharge process while being able to grow from selected hydrocarbons [11]. Earlier studies determined that CNT immersed in suitable base fluids had the ability to reduce erosion and clogging which is seen in micro particles and this has led to significant energy savings and high efficiency in micro-channels [11],[13],[14]. The knowledge of the thermal conductivity of CNTs is very useful in the design of nanoelectromechanical systems (NEMS) and microelectromechanical systems (MEMS) used for efficient thermal transport system in electrical, mechanical and chemical applications, solar energy systems and central air conditioning systems. It is also necessary in the development of molecular theories in nanofluids and nanofluid mixtures [15]. Low thermal conductivity are presently a major disadvantage in the synthesis of heat transfer fluids with high energy-efficiency needed for very high performance cooling [11]. Nanofluids however, are seen to have high thermal conductivities which depends not only on forces acting on nanoparticles but also on particle motion and interaction with turbulent eddies which leads to an astonishing reduction in heat exchanger pumping power [13]. After reviewing previous works, we find that the reported thermal conductivities of CNT is as high as 3000W/mK [16]. For bio-based CNT on the other hand, there is less literature available. Recently, the thermal conductivity of bio-based phase change (PCM) was enhanced by adding carbon nanotubes and the thermal conductivity reported is 0.557W/mK [17]. In comparison to tested carbon black, studies by [18] revealed a 36% in the thermal conductivity of carbonized ball milled lignin after synthesis by ball-milling. This review presents the various methods of synthesis of carbon nanoparticles and equally important, an investigation of the thermal conductivity measurements of MWCNT and SWCNT. The effects of temperature, length, substrate and diameter of the nanotubes have been analyzed. The current trend towards miniaturization and the global need for a renewable and sustainable heat transfer source has motivated this study.

2. Synthesis of Carbon Nanoparticles

The tube diameter (d) and the helical angle θ are the two factors that describe the structure of a nanotube, not to forget the helical vector $\mathrm{C} = \mathrm{na}_1 + \mathrm{ma}_2$ (where a_1 and a_2 are the graphene sheets). Tubes are characterized by (x,y) notation depending on how they are rolled. The diameter and helical angle of nanotubes can be found from x and y [11] and given in equation (1) and equation (2).

$$d = \frac{c}{\pi} = \frac{\sqrt{3r_{c-c}}(y^2+xy+x^2)^{1/2}}{\pi} \tag{1}$$

$$\theta = tan^{-1}\frac{\sqrt{3m}}{(y+2x)} \tag{2}$$

r_{c-c} The c-c distance of the graphene layer (1.421Å)

C Length of the chiral vector

From a broad view, there exist three methods of synthesizing carbon nanotubes [11],[19],[20]:

a. Formation of single-walled nanotubes (SWNT) by the incorporation of transition metals in catalytic amounts in the arc-discharge process;
b. Laser evaporation which forms nanotubes with rope-like structures; and
c. Chemical vapor deposition.

Bio-based carbon nanoparticles are a promising substitute for the metal based nanoparticles. Past studies on CNTs have shown increase in thermal conductivity, latent heat, thermal resistance, environmental friendliness, renewability and overall thermal efficiency [17],[18],[21-23]. Synthesis methods for CNT production depends largely on its application. The precursor used during synthesis is important in governing the yield and morphology of carbon nanoparticles. Precursors like petroleum pitch, graphite powders, carbon rich polymers, petroleum pitch, and other types of hydrocarbons have been successfully used in synthesizing CNT and research is still ongoing in this area, [11, 24-28]. However due to toxicity and environmental hazards that can be caused, it is important to produce nanomaterials which are free from amorphous carbon. They should be obtained from green sources that would pose no harm to humans and the environment.

The authors in [29] reviewed greener routes used for nanoparticle production. Greener routes sourced from plant extracts and natural products used in past research were studied. These natural products, some of which were used as capping agents and reductants during synthesis have proven to assist with problems relating to environmental contamination, while using non-toxic solvents like water. Parts of plants like the roots, leaf, fruits, stem and seeds are being adopted for synthesis of nanoparticles from metallic nanoparticle synthesis. [15, 29-33]. This is identified to be due to the presence of polyphenols because they are stable in acidic solutions and they also modulate the oxidative defense system in cells [34]. The bio-molecules present in plant are reported to reduce metal ions or act as capping agents to particles in nano-size in a one-step green synthesis methods developed by [33]. The authors emphasized their advantages of being readily conducted at room temperature, easily scaled up and rapid. Micro-organisms have been used to synthesize nanoparticles; however the rate at which production occurred was found to be slow and only limited number of sizes and shapes are amenable compared to that of biomass-based. The polyphenols contained in tea extracts can act as both reducing and chelating agents which prevents agglomeration in nanoparticle formation and consequently leads to an increase in stability and longevity [29].

Authors [21] and [35], synthesized carbon nanoparticles from glucose and alkali or acid additives. However the former carried out their experiments under ultra-sonication condition, while the latter utilized hydrothermal synthesis. From their results, the method based on ultrasonic synthesis was more efficient in terms of particle size agglomeration as the particle size obtained (5nm) as opposed to the particle sizes from [35] which was 70-100nm. Ultrasound has been known to produce alternating high pressure and low-pressure waves in solution, resulting in the collapse and formation of small vacuum bubbles [21]. Zhang et al. [22] have also applied a simple hydrothermal method using L-ascorbic acid as a carbon source. There were no acidic additives and there was no need for any surface modification. However, the addition of ethanol enhanced the surface state of the carbon nanoparticle. Gonugunta et al. [36] studied the production of bio-based carbon nanoparticle using lignin as the carbon source. The freeze drying process was used in order to avoid lumps or aggregates formed from carbonization. It was observed that there was an increase in thermal stability with a corresponding increase in KOH. This was as a result of the influence of KOH on the particle size as lignin samples modified with KOH yielded ultrafine particles even though it forms agglomeration at higher concentrations of 15% [36]. To avoid the problem of lump formation (agglomeration) which usually arises from carbonization, thermal pyrolysis method was recently used by Roshni and Ottoor [37] to synthesize bio-based nanoparticles from coconut milk. The authors used the pyrolysis method because it does not involve any surface passivating agent or any acid treatment. The result however shows a large size range (20nm-50-nm) which could be due to non-homogeneity in the pyrolysis method adopted. Apart from the chemical methods used for synthesis, physical approaches are also being used for synthesis of nanoparticles [18, 27, 38, 39]. Physical methods include: ball milling and mechanical grinding. A bottom-up mechano-chemical approach using milling of inorganic precursors was also reported by Rak et al. [27]. Conventionally, ball milling is a top down approach because the particles are broken down into nanometer sized particles.

A. *Effects of synthesis parameters on the growth of CNT*

The parameters involved in the synthesis of CNT plays a significant role on the final characteristics of the CNT structures. The influence of synthesis time on CNT yield from literature increases with increasing time [40-44]. This is evident from studies by Niu et al. [40], where at 2 minutes, isolated and short SWCNT with high defects and poor quality were obtained while CNTs with lesser defects where achieved for synthesis carried out in 30 minutes. Conversely, it has been observed that CNTs obtained after much longer synthesis time were likely to possess weaker crystallinity [42]. This report stated that increasing the reaction time of synthesis led to a constant inner diameter while the outer diameter increased. The effect of temperature on synthesis of CNT using nickel substrates generated results which points toward a major synthesis of MWCNT at lower temperature and nickel thickness [45]. The temperature was varied between 900ºC, 800ºC and 700ºC and the varied temperatures formed radical results in the CNT structure produced. The study showed that higher temperatures supports core-shell configuration and for declining temperatures, the formation of CNT is enhanced. Toussi et al. [44] showed that when the temperature of synthesis is lower than 750ºC, CNT formation was lesser; however CNT formation was higher for higher temperatures (>900ºC). The best temperature for CNT growth by Toussi et al. [44] occurred between 800ºC and 900ºC and the optimum growth temperature was at 850ºC , while Shamsudin et al. [46] obtained an optimum growth of about 99.99% at 900ºC. Apart from synthesizing from high temperatures, carbon nanotubes can also be synthesized from carbonaceous solids at low temperature (450ºC) [47].

In the chemical vapor deposition (CVD) method, a hydrocarbon gas which is the carbon source is used together with a metal catalyst that acts as seed for the development of CNTs. CVD takes place at a lower temperature (500-1000ºC) [11]. Synthesis of CNTs is usually followed by purification, deposition and suspension in an organic solvent [12]. Using CVD method of synthesis allows more precision control of CNT orientation, lower cost and more defined product(s). The electrical properties of CNT's have been improved by synthesizing SWCNT using CVD on supported catalyst. They have proven to be semiconducting in nature and also quasi-metallic with small band gaps [20].Selecting a proper precursor, catalyst and suitable vapor pressure optimizes the yield of growth rate and quality of produced CNTs [48].

The choice of catalyst and substrate is important for the successive growth and desired orientation of CNTs [49]. The use of transition metals as catalyst for CNT synthesis have been reported by [50-52].The most common transition metal catalysts used are Ni, Co and Fe due to their extraordinary solubility and carbon diffusion rate. They are desirable due to high melting points and strong adhesion qualities. Higher quality nanotubes growth is obtained when Fe is used as catalyst during synthesis compared to Co and Ni. This has been attributed to its greater carbon solubility. Increasing the Fe quantity decreases the quality of the nanotubes synthesized due to general aggregation of the Fe particles. It was concluded that lower metal loading percentage is preferable for the production of better quality CNTs with identical diameters [53]. MgO and Mo have also been recognized to be an appropriate catalyst support for Fe as it produces nanotubes with enhanced graphitization, smaller and more uniform nanoparticles [50, 51]. A uniform diameter CNT was synthesized using Mn_{12} as a catalyst precursor [54]. The diameter grown is 1.5±0.31nm and the result indicates that an adhesion strength exists which can determine the diameter of as-grown SWCNT needed for controlled synthesis [54]. Cheng et al. [55], revealed that the dimension of the catalytic particles and amount dispersed on the support was useful in controlling nanotube shape. A novel method of synthesis was reported by the authors using an improved floating catalyst approach produced by catalytically pyrolizing benzene at 1100ºC-1200ºC [55].

Solid organo-metallocenes are have been used due to their metal liberating qualities which catalyzes hydrocarbon deposits efficiently [48, 56]. Alloy of metals also play a substantial role in catalyzing the growth CNTs and through them a better yield of CNTs are derived [57-60]. As more research continues on enhancing the growth of CNTs, noble metals have been discovered to effectively synthesize CNTs. However, they are most effective when their particle sizes are very small (<5nm) [48]. A robust and cost effective method of CNT synthesis was reported by Jeong et al. [17], in which catalytic particles solution and carbon sources were atomized without the use of a special heating system. This method of synthesis proved more effective than thermal pyrolysis based catalytic vapor deposition (CVD) in which there is difficulty in controlling the quantity of particles entrained in carrier gas due to steep temperature gradient between furnaces. The method also proved more effective than aerosol pyrolysis [17]. Catalytic pyrolysis involving annealing of carbonaceous solid containing cobalt has been used to synthesize MWCNT [47]. The cobalt is used as a catalyst to decompose carbonaceous solid, form carbon gas species and eventually growth of CNTs. The use of cobalt can also lead to the deposition of carbon at high temperatures and are hazardous [51]. This mentioned downside of cobalt and other transition metals motivated Abdullahi et al. [51] to use a systematic approach based on catalyst loading, pre-treatment and selection of the right operating conditions for the improvement of a monometallic catalytic system for the growth of SWCNT. High quality SWCNTs with high yield was achieved by using a 2 wt.% Fe–MgO catalyst with diameters ranging from 0.8-2.0nm.

Understanding the growth and controlling the diameter of CNT facilitates the research of new applications and basic properties of CNTs [20, 61]. The major function of a catalyst in describing the nanotube diameter synthesized by chemical vapor deposition can be seen from the investigation of the diameter distribution which shows a close connection between diameters of nanocluster nanotubes and catalysts [61]. This discovery was made when the authors Cheung et al. [61] prepared iron nanoclusters having three distinctive diameters which were utilized in the development of CNTs with comparable diameters. Diameter-controlled synthesis of SWCNT using Mn_{12} cluster as a catalyst precursor by means of mist flow CVD has also been reported by Sun et al. [54]. The mist flow CVD was reported to be effective for the diameter controlled growth of SWCNTs. Site selective synthesis based on CVD is able to grow CNTs at controllable locations and with desired orientations on surfaces [20]. CVD are described to be effective in the production of materials which are hybrid in nature and based on CNT from various supports where superficial located growth is desired [49]. The study was on the comparison and utilization of synthetic hematite and natural nontronites as interface adaptation nanoparticles for local growth of carbon nanotubes at required support.

3. Thermal Conductivity of Carbon Nanotubes

A. *Thermal conductivity in a base fluid*

Thermal conductivity and heat transfer of nanofluids depends not only on the forces acting on nanoparticles, but also on particle motion and interaction with turbulent eddies [14]. Convective heat transfer can be passively improved by altering the boundary conditions, flow geometry or by increasing the thermal conductivity of the base fluid [62]. Decrease in diameter of nanoparticles brings about a more uniform temperature distribution. However, this leads to a corresponding increase in cost and complexity of nanoparticle production [63]. Previous study reveals that the thermal conductivity of fluids with sphere-shaped particles improved with an increase in the ratio of the surface area to volume ratio of the particle and volume fraction of the particles [13]. It has also been pointed that since transfer of heat takes place at the surface, nanoparticles with a wide surface area should be used. Compared to micrometer and millimeter-sized particle fluids, nanofluids have enhanced rheological properties and extended stability which makes them possess increased thermal compatibility [64]. Carbon nanoparticles are being utilized in the enhancement of the thermal conductivity of their applications [17, 64-67]. The high aspect ratio of CNTs, their special surface area and high conductivity is responsible in making them suitable for heat transfer purposes in nanofluids [64, 66]. The improved thermal conductivity is due to a well formed arrangement at the solid/liquid interface and the mode of heat conduction in nanotube suspensions [64]. Brownian motion has also been suggested to be a major phenomenon in controlling a nanofluids thermal conductivity [64].

The study by [17] considered the preparation of thermally enhanced bio-based phase change materials (PCM) by utilizing a method known as vacuum impregnation with exfoliated graphite nano-platelets. The results show a 375% improvement in thermal conductivity. There was also an improvement in the latent heat and thermal resistance. Nanomaterials added to a working fluid in a vapour compression cycle was theoretically and experimentally tested for performance and an increase of 10.5% was observed with 13.5% less energy consumption [68]. The thermal conductivity of synthetic engine oil and ethylene glycol were improved by dispersing multi-walled carbon nanotubes and measurement was carried out using the transient hot wire method [64]. The authors stated an enhancement in thermal conductivity with an increase in volume fraction. Thermal conductivity enhancements up to 12.4% was achieved for CNT/ethylene glycol suspensions at a volume fraction of 1 vol% when compared to CuO based nanoparticles. In addition, up to 30% thermal conductivity enhancement was achieved for CNT-engine oil suspension with 2 vol%. These outcomes evidently point to the fact that there exists an enhanced thermal conductivity ratios improvement with a corresponding rise in the volume fraction of CNTs and it is almost non-linear [64].

B. *Thermal conductivity of MWCNT*

The need to measure the intrinsic thermal properties and thermal conductivity of individual carbon nanotubes in order to get an accurate estimation prompted the study by Kim et al. [16] and Choi et al. [69]. The studies of the thermal properties of MWCNTs by taking bulk measurements had a disadvantage of yielding a joint average in a sample made of different tubes. This is as a result of the existence of various tube-tube junctions which can be an obstacle to thermal transport in bundle nanotubes [16]. These tube-tube interactions are primarily created from van der Waals forces with an exception for unique instances when local charge introduce additional electrostatic fields [70]. It was proposed that the nanotubes should touch each other over less than 2-3% of their total length in order to achieve high thermal conductivity in long MWCNT [70]. A hybridized device with MWCNT to investigate thermal transportation was developed by Kim et al [16]. A mechanical approach was used to place MWCNT on the device and this approach produced a device of nanotube structure which has the ability to quantify the thermal conductivity of individual MWCNT. The thermal conductivity reported is over 3000W/mK at room temperature. On the other hand, Choi et al. [69] placed a single CNT across the electrodes for thermal conductivity measurements using 3-ω using a combination of electric fields with an alternating current and direct current. This approach is based on selective deposition technique which has a benefit of permitting the control of single nanotube placement. The thermal conductivity was reported as 650 and 830 W/mK respectively. The technique is reported to operate on a narrow-band detection technique and is said to give better signal-to-noise ratio [71]. In order to produce reliable data on the thermal conductivity of different nanotube sizes, an outstanding measurement technique was developed based on the four-point-probe third-harmonic (3- ω) method with assistance of a focused ion beam (FIB) for electric field supply [72]. When likened to the two point probe 3- ω technique used by Choi et al. [69], the precision of the measurement is considerably improved by disregarding the contact contribution in the measurement which was previously done by annealing the nanotube samples at 600^{o}C. The measured value for the CNTs investigated by the authors in [72] is 300 $\pm$ 20 W/mK. The variation in thermal conductivity is likely to depend on the size and type of carbon nanotube employed which results in diverse mean free paths of the energy carriers. The 3- ω technique of measuring thermal conductivity recently used by Vollebregt et al. [73], was employed to determine the thermal conductivity for a low temperature grown vertical MWCNT bundles. This is important because CNT bundles which are required to obtain a low electrical and heat resistance applications need to possess low thermal conductivity. The thermal conductivity reported was 1.7-3.5 W/mK. The disadvantage of this method is a low quality sample arising from a low growth temperature.

The notable technical difficulty in fabricating devices used by the authors from literature [16, 69, 71, 72], motivated the research by Xie et al. [74]. The authors made an estimate of the thermal conductivity of individual CNTs from the obtained thermal diffusivity measurement of MWCNT array based on a laser flash technique. The following correlation was used to determine the thermal conductivity [74]:

$$\lambda = \alpha \rho C_p \tag{3}$$

Where:

C_p Specific heat;

ρ Density; and

α Thermal diffusivity of CNT.

The thermal conductivity at room temperature was reported to be about 750W/mK and it increased smoothly with an increased temperature. Measuring the thermal conductivity of a film of MWNTs using pulsed photo-thermal reflectance technique was used by Yang et al. [75] and Samani et al. [76]. This non-contact method is said to have an advantage of having no boundary scattering due to reservoir junction which was detected in electrical junction [76]. The thermal conductivity for CNT bundle length of 10 – 50 μm and diameter 40-100 nm was measured and was found to be about 15W/mK [75] while Samani et al. [76] reported a thermal conductivity of 2586 W/mK for an individual CNT of length 2 μm and diameter 150nm. The high thermal conductivity of the individual MWCNT by Samani et al. [76] has been proposed to arise from the existence of ballistic flux of long-wave acoustic phonon, which originates from all the walls having equal contribution to thermal transport. These phonons enable heat transport in MWCNT, and are therefore an essential factor of the thermal conductivity. For novel materials for which quantitative measurements cannot be carried out, simulations involving molecular dynamics are applied. The need to comprehend the lattice thermal transport properties of carbon nanotubes for nano-electromechanical systems (NEMS) and microelectromechanical systems (MEMS) devices prompted the study by Che et al. [77] and Berber et al. [78]. The molecular dynamics (MD) approach is critical to note the influence of various defects speculative calculations and the thermal conductivity of CNT. One major concern of using MD however, is the effect of size of the simulation box as a result of the periodic boundary simulations [77]. The thermal conductivity is extracted from the Green-Kubo relationship in (4).

$$\Lambda(w) = \frac{1}{2\kappa_B T^2 V} \hat{C}^{q}_{jj}(\omega) \tag{4}$$

Where:

κ_B Boltzmann constant;

V Volume;

T Temperature of the sample; and

$\hat{C}^{q}_{jj}$ Quantum canonical correlation function.

The thermal conductivity obtained was 950 W/mK along the tube axis and 5.6 W/mK in a perpendicular direction to the tube.

C. Thermal conductivity in SWCNT

The thermal conductivity of SWCNTs from most studies in literature have been seen to depend on several CNT parameters ranging from nanotube length, simulation method for free boundary and periodic boundary conditions [79, 80]; temperature [81, 82]; axial strain [83]; radius and chirality of the tube [84], defect influence [77] and interaction between the nanotube with the substrate [85]. Several other studies also emphasized the fact that dependence of thermal conductivity below 30K is reliant on phonons rather than electrons [81]. Table 1 lists the thermal conductivity and measurements of SWCNT from literature.

Table 1. Thermal conductivity of carbon nanotube from literature

Author	**Thermal conductivity technique**	**Result**
Hone et al. [81]	Measured using a comparative method. Temperature drops are measured using constatan rod.	Room temperature thermal conductivity of 1750-5800W/mK
Che et al. [77]	Empirical bond under dependent force field, based on equilibrium molecular dynamics simulation.	950W/mK (Nanotube bundle along tube axis) 5.6W/mK (nanotube bundle perpendicular to the tube)
Silotia et al. [86]	A suitable form of relaxation time that represents phonon-phonon scattering and interaction with an appropriate anisotropic dynamical model.	At increased temperatures thermal conductivity in SWNT ropes tends towards that of a two-dimensional material while at lower temperatures, it behaves as a quasi-two-dimensional material because of the curvature of graphene sheets
Duzynska et al. [87]	Optothermal technique.	26W/mK at 300K 9W/mK at 450K
Li-Jun et al. [88]	Physical property measurement system (PPMS, from Quantum design Corporation).	650W/mK at 100K decreases to 480W/mK and keeps almost constant from 100-300K
Osman and Strivastava [89]	Molecular dynamics simulations.	The thermal conductivities beginning from 100K first show a peaking behaviour after which it drops off at higher temperatures.
Gu and Chen [90]	Analysis of all possible combining and splitting Umklapp scattering process based on total phonon dispersion relations.	474W/mK at 300K
Berber et al. [78]	Molecular dynamics simulations using the Tersoff potential, augmented by Van der Waals interaction in graphite.	6000W/mK at room temperature for an isolated (10,10)
Pan et al. [91]	Non-equilibrium molecular dynamics method with Brenner II potential.	The thermal conductivity at 300K of (10,0) is 237W/mK
Lukes and Zhong [79]	Molecular dynamics simulation	Thermal conductivity improvement with nanotube length, from about 10 W/m to 375 W/m K
Pop et al. [92]	Joule self-heating.	3,500W/mK at room temperature
Saavin et al. [85]	Molecular dynamics simulations centered on the green Kubo formalism.	360W/mK and 88W/mK

Hence, an in-depth knowledge of the principle of conduction of heat in SWCNTs comprises studying the variance between the different phonon modes and to determine which types of phonon modes play the governing role.

D. Temperature dependent thermal conductivity of single-walled carbon nanotubes

The thermal conductivity of SWCNT measured by [81] was focused on the low temperature range (<100K), which had a linear behavior. At this low temperature, a small diameter most probably affects the phonon properties of single-walled carbon nanotubes [81, 82]. A significant decrease in thermal conductivity was observed as the temperature decreased (Fig. 1). The results from the studies revealed an intrinsic thermal conductivity of nanotube bundles rather than sample dependent effects like joints between bundles. Cao et al. [82] reported a peak behavior at about 85K accompanied by a rapid decrease in the temperature dependent thermal conductivity which is caused by the Umklapp scattering freezing out. The peak behavior will shift to higher temperatures as diameter increases while neglecting dependence on tube chirality [89]. This is because as the temperature improved, the Umklapp scattering which is strong becomes more effective due to the thermal population of higher-energy phonons (Fig. 2) [82].

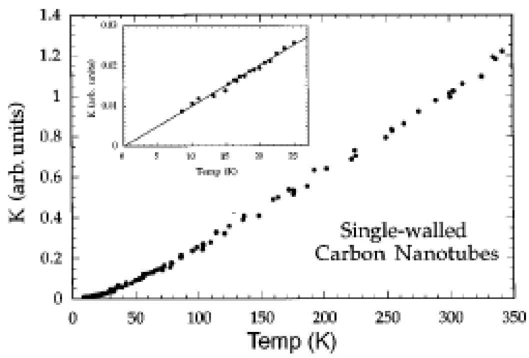


Fig. 1. Thermal conductivity of SWNT as a function of temperature [81].

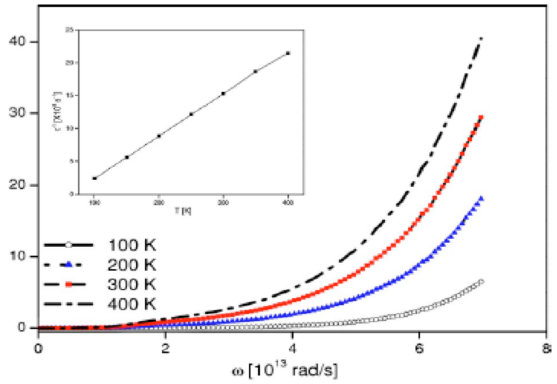


Fig. 2. Relaxation rates of Umklapp process of (6,0) SWNT [82].

Silotia et al. [86] attempted to make an explanation of the experimental variation in temperature in the thermal conductivity stated by Hone et al. [81] using a theoretical anisotropic model. The thermal conductivity centered on the studied model is given as:

$$\kappa = \frac{B_c^2 \theta_{D.eff}^2}{\hbar^2 (6\pi^2 n)^{2/3}} \frac{\pi\hbar}{B_c} \theta_{D.eff}^{d-1} \frac{1}{3} \times I \tag{5}$$

Where: $\hbar$ is the Planck's constant, B_c is Boltzmann constant and $\theta_{D.eff}$ is the efficient temperature. The anisotropic model is used because other models like Debye and the extended Debye model do not take into account the presence of the anisotropic nature of SWCNT especially at low temperatures below 30K. In addition, the anisotropic model illuminates in detail the variation in temperature of specific heat for the entire temperature range of 2-300K [86]. The thermal conductivity involves phonon-phonon interaction and phonon-phonon scattering that produces phonon relaxation time τ or phonon mean free path l. Figure 3 shows the thermal conductivity measurements by [86]. From the Figure, it is observed that the highest thermal conductivity was observed at the highest temperature (350ºK) and the lowest conductivity at the lowest temperature (8ºK).

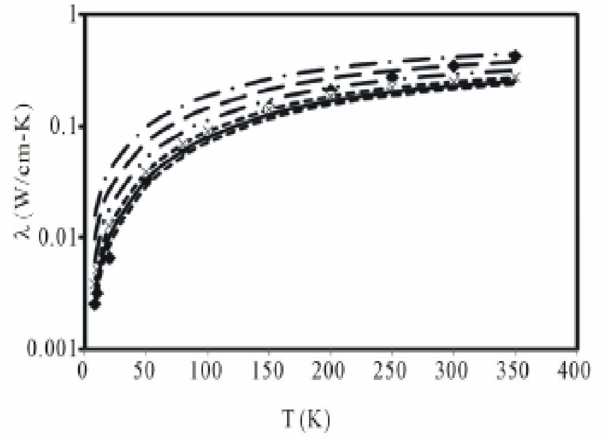


Fig. 3. Thermal conductivity of SWCNT in the temperature range 8-350 at different diameters (0.7, 0.75, 0.8, 0.9, 1, and 1.1,) [86].

At 100K, a clear peak was observed in the study carried out by Li-Jun et al. [88], which gradually decreases with an increasing temperature till it gets to 200K and from 200K-300K, the temperature becomes constant. This behavior is said to be due to the temperature dependent property of phonon. At low temperature, the phonon relaxation time is inversely proportional to the temperature which translates into a decrease in thermal conductivity with increasing temperature. However at high temperatures, phonon-phonon scattering contributes to the phonon-decay and shows no temperature dependence (the thermal conductivity is constant) [88]. This peaking behavior is also seen in the studies by Osman and Srivastava [89]. It was observed by the authors that the peak changes to greater temperatures with increasing diameter of nanotube which is due to the beginning of Umklapp scattering, which is said to lower the thermal conductivity at greater temperatures, and also depends on nanotube radius. The peak in this study occurred at 400K and then a drop followed at 500K. Recently a technique known as opto-thermal method was used to determine the intrinsic thermal conductivity and interfacial thermal conductance on thin nanotube films deposited on silicon substrates as a function of temperature in the range 300-450K [87]. The tube diameter was in the range of 1.2-1.7nm with a mean length of 1μm. The value of K was found to decrease non-linearly by nearly 60%. This was due to the increase of multi phonon scattering at higher temperatures. The thermal conductivity decreased from 26.4 to 9.2W/mK in the temperature range of 300-450K.

The thermal conductivity in higher temperature range of 300-800K has been determined by [92] using reverse fitting based on an existing electro-thermal transport model. The results indicated a restrained decrease in the thermal conductivity of SWCNT close to the extreme end of the temperature range inversely proportional to T^2. The presence of Umklapp phonon-phonon scattering that leads to a temperature dependence of 1/T is seen from the graph. In addition, at the upper end of the graph can be seen a drop in thermal conductivity at a rate sharper than 1/T. The reason given to this is the effect of second order scattering process with scattering rates proportional to T^2. At the low end of the temperature range, a levelling of thermal conductivity was observed signifying a shift towards thermal transportation restricted by phonon boundary scattering as a result of the limited sample size as seen in Fig. 4.

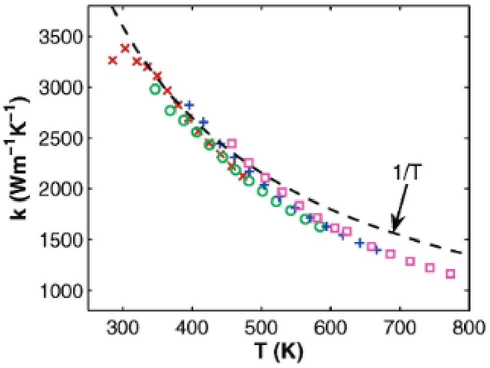


Fig. 4. Thermal conductivity of SWCNT in the temperature range 300-800K [92].

4. The Effect of Substrates on the Thermal Conductivity of SWCNT

The question arose on whether the thermal conductivity of SWCNTs was related to the effects of substrates [85]. This question was answered by carrying out a straight modelling of the heat transfer by using molecular dynamics models and also by studying the equilibrium multi-particle dynamics which is centered on the Green-Kubo formula. The study discovered a finite conductivity for nanotubes that were placed on substrates unlike remote carbon nanotubes that displayed an unusual thermal conductivity. The mean free path that is conducted by heat is larger or of the same order for the Knudsen number (*Kn >1*) and of the nanotube length. This show the relations of CNT with a substrate can radically alter the character of thermal conductivity which is as a result of the presence of a constricted gap at the extremity of the frequency spectrum of acoustic phonons.

5. The Role of Phonon-phonon Scattering in Carbon Nanotubes

Heat conduction by phonons is an general process that encompasses an extensive scope of physics and plays a critical role in applications ranging from LED lighting to space power generation [93]. Acoustic phonons play a dominant role in phonon state [81, 82, 92]. Additional phonon mode, scattering process and rolling-up of graphene sheets have major outcome on the temperature dependence of the thermal conductivity at both high and low temperature [81, 86]. In a perfect isolated SWCNT, an analysis of the physical mechanics can be carried out using phonon relaxation rate which is majorly controlled by three-phonon Umklapp scattering process and boundary scattering [82, 90]. The Umklapp process is made up of the combining process and the splitting process which both contribute to thermal resistance. The total relaxation time can be derived from Matthiiessen's rule and given as [82]:

$$\frac{1}{\tau} = \frac{1}{\tau_B} + \frac{1}{\tau_U} \tag{6}$$

With$\frac{1}{\tau_U} = \frac{1}{C_p} + \frac{1}{S_p}$,

Therefore the total relaxation rate can be rewritten as:

$$\frac{1}{\tau} = \frac{1}{\tau_B} + \frac{1}{C_p} + \frac{1}{S_p} \tag{7}$$

Where τ_U is the three-phonon Umklapp scattering process and τ_B is the relaxation time for boundary scattering. It was observed that there exists additional low lying doubled over phonon subdivisions as the tubes diameter increases which invariably contributes to thermal conductivity. The use of complete dispersion relations for SWCNT by Gu and Chen [90], concentrated on the three-phonon interactions to derive thermal conductivity. Han [94] has shown that the relaxation rate of Umklapp process is obtained from the given lattice characteristics and dispersion data. Because the role of low frequency phonon is more intense compared to that of high frequency, the combining process has been assumed to be of greater importance than the splitting process in the assessment of thermal resistance.

The combining process and the splitting process respectively satisfy the selection rule:

$$q + q' = q'' + G \tag{8}$$

$$q = q' + q'' + G \tag{9}$$

Where q,q', q'' are phonon wave vectors and G is the reciprocal-lattice vector [90]. From equation (9), the rate of relaxation for the three-phonon Umklapp process can be given as [90]:

$$\frac{1}{\tau} = \frac{4h\gamma^2}{3\rho_l v^2} \sum_{j'=1-N/2}^{N/2} \sum_{p'=1}^{6} \frac{\omega\omega'\omega''}{v_g} \delta(\delta_\omega) N(\omega', \omega'') \tag{10}$$

The thermal conductivity calculated for the tube was found to be 474 W/m K at 300 K. The outcome of orderly functionalization on the thermal conductivity of SWCNT at 300Kwas carried out by [91] using a non-equilibrium molecular dynamics (NEMD) simulations. The simulation was carried out to find the character of the thermal conductivity by means of decorated hydrogen atoms. This was done by calculating the phonon power spectra of the SWCNTs from Fourier transform of the velocity autocorrelation function. From Fourier's equation, the thermal conductivity is defined thus:

$$J = -\lambda \nabla T \tag{11}$$

Where: T and J is the resulting heat flux density and ∇T is the gradient of the temperature. The results show that the functionalized CNTs show considerably lesser thermal conductivity than pristine CNT (CNT with attached hydrogen). It was also ascertained that there exists more repressed axial phonon modes of the unsystematically functionalized SWCNTs than the systematic functionalized tube. The atoms of hydrogen which attach to the CNTs act as defects which consequently decrease the thermal conductivity. The study of the phonon spectra shows that the density of phonon modes is considerably altered for functionalized tubes, which leads to the suppression of some vibrational modes and a decrease in the length of phonon scattering. This results in the degeneration of thermal conductivity. At room temperature, the phonon-phonon Umklapp scattering is negligible and therefore the phonon transport is nearly ballistic with the phonons having only a small number of scattering events between the thermal reservoirs. This feature is not present in bulk measurements of MWCNT which is conceivably because of the added extrinsic phonon scattering mechanisms like tube-tube interactions [16].

6. Viscosity of Carbon Nanotubes Based Nanofluids

Since the advent of carbon nanotubes, it has been shown that the thermo-physical properties of base fluids like water and ethylene glycol can be enhanced by adding carbon nanoparticles in precise quantity. Nanofluid viscosity is a crucial property for uses involving flow of fluid and it determines the pumping power [95]. Changing the viscosity of a base fluid by adding nanoparticles can lead to a direct impact of the systems overall efficiency. The viscosity of CNT nanofluid is dependent on the temperature, shear rate for different nanotube concentration and agglomeration effects on rheological characteristics [96].

Table 2. Viscosity measurements of CNT nanofluid from literature

Author	**Viscosity measurement technique**	**Temperature**	**Results**
Sadri et al. [97]	Rotational rheometer	15,30 and 45^{o}C	Nanofluid viscosity improved with increasing sonication time up to a maximum value and then decreased with further increase in sonication time.
Halefadl et al. [95]	Stress controlled rheometer in a cone and plate configuration.	40^{o}C	Results show that the shear viscosity increases with nanotube concentration for a specific shear rate
Jo and Banerjee [96]	A rotational rheometer and a cone and plate test.	Fixed temperature of 550^{o}C	Nanofluid viscosity is significantly enhanced up to 93% in the concentration of 2wt%
Aladag et al. [98]	Stress controlled rheometer	2-10^{o}C	Viscosity of the CNT suspension decreases when the shear rate increases
Vakili-Nezhaad and Dorany [99]	Bohlin CVO rheometer (Malvern Instrument).	Between 24^{o}C and 100^{o}C.	Enhancement of the viscosity index is 14.11%

A. Shear rate and temperature effects on the viscosity of CNT nanofluids

The study by Aladag et al [98] investigated the influence of temperature on viscosity for CNT/Water and Al_2O_3/Water nanofluids at small concentration and for a temperature range of 2-10^{o}C. The effect of pressure drop and viscosity is important and should to be taken into consideration when used in low temperature application like air conditioning systems. The rheological study was carried out by observing the hysteresis phenomenon. The results showed that viscosity increased when the temperature decreased as shown in Fig. 5, and also the behavior of the CNT suspension was described as non-Newtonian shear thinning fluid when observed in the experimental condition of the study. Similarly results by Sadri et al [97] indicates a decline in viscosity when temperature was increased (Fig. 6). The study [97] also reported that MWCNT/water based nanofluids behaved as a non-Newtonian fluid. This is because the dynamic viscosity differs as a result of an increase in shear rate. The result of shear thinning effects from the two studies discussed can be credited to realignment of the clusters in the direction of the shearing flow due to the formation of primary particles and the de-aggregation of the nanotube clusters leading to a less viscous force [98],[95].

A recent study has shown that using molten salt as base fluid was advantageous for high temperature applications like concentrated solar power (CSP) [100]. This gave way to the studies by Jo et al [96], who investigated the rheological behavior of CNT dispersed in molten salts under high temperature. A highly non-linear rheological behavior was observed, typical of shear a thinning liquid which was more distinct for increased mass concentrations of the nanoparticle. A non-Newtonian behavior was observed in low shear rate region, consistent with literature. The viscosity of the base fluid was significantly enhanced by doping MWCNT which is likely attributed to the agglomeration of the nanotubes [96].

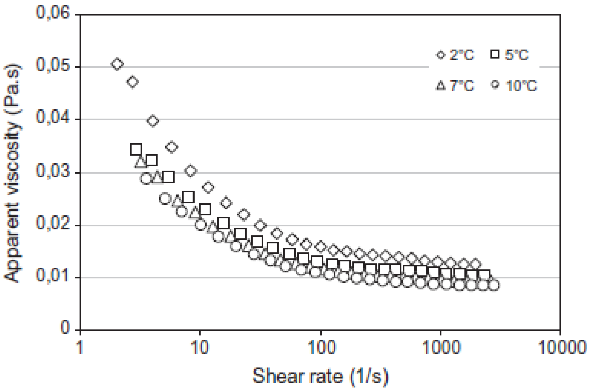
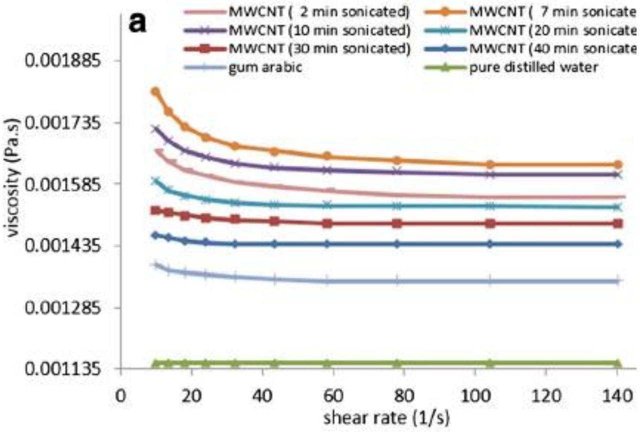
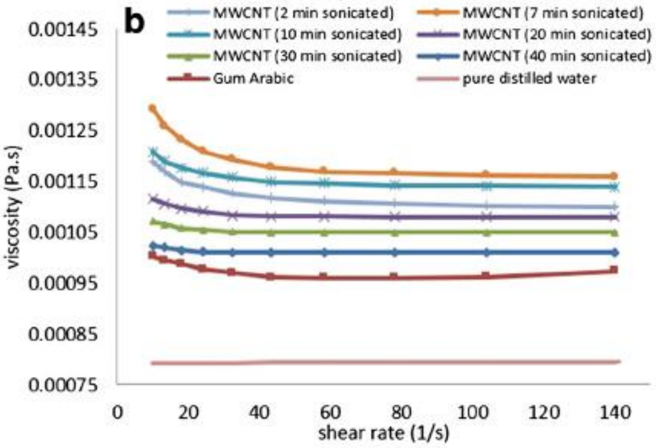


Fig. 5. Influence of temperature apparent viscosity versus shear rate of CNT nanofluid [98].





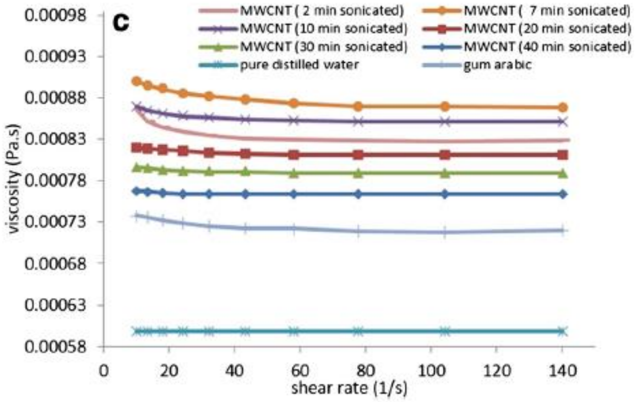


Fig. 6(a,b,c). Dynamic viscosity vs shear rate at various times of sonication [97]

B. The role of surfactant on the viscosity of CNT

Halelfadl et al [95] reported results on the experimental investigation on the rheological properties of CNT water based nanofluids stabilized by sodium dodecyl benzene sulfonate (SDBS) as surfactant. The shear viscosity of the base fluids slowly decreases with the decrease of SDBS volume fraction.

C. The effect of particle volume fraction on the viscosity of CNT nanofluid

Nanofluids sample prepared from volume fraction 0.278%, 0.111%, 0.055% and 0.00555% respectively tested at 20,30 and 40ºC respectively shows that nanofluids with particle concentration of 0.278% and 0.111% behaved as shear thinning fluids [101]. The shear thinning region was up to 200S^{-1}; for higher shear rate, the viscosity tends to a Newtonian plateau. For lower particle content (0.055% and 0.0055%) however, the nanotube behaved in a Newtonian manner [101]. Experimental results by Vakili Nezhaad [99] shows that the kinematic viscosity of nanofluids was improved with decline in the temperature and increase in the concentration of MWCNT concentration. It was also pointed out from the studies that a non-linear relationship existed between MWCNT concentration, viscosity and temperature.

7. Discussion and Conclusion

Carbon nanotubes undoubtedly are an intriguing next generation materials, which are being continuously improved upon for application in diverse areas including chemical, mechanical and electrical systems. Their synthesis, growth and application is an area of active research.

From literature, significant milestones have been achieved in the field of CNT synthesis with a focus on CVD. Synthesis parameters have been shown to have a direct output on the shape and morphology of as-grown CNTs. The parameters include precursor, synthesis time, temperature, diameter, among others. The inconsistent heat transfer properties such as thermal conductivity of CNTs are attributed to the various conditions such as temperature, diameter, length, and the morphology of growth of the CNT. The present review validates the similarities in the thermal behavior of MWCNTs and graphite. The thermal conductivity of multiwalled carbon nanotubes can be modelled by making assumptions on the parameters and properties of graphite, even though it is probable that the interlayer coupling in multiwalled carbon nanotubes could be different than it is in graphite. It was also presented that the phonon confinement effects in MWCNTs are significant only at very low temperatures. At these temperatures, the thermal conductivity in SWCNT is dominated by phonon boundary scattering. A linear temperature profile exists at low temperatures less than 80K but shows peak behavior at 85K and falls off at higher temperatures.

Past studies on viscosity shows that viscosity can be enhanced by increasing the CNT concentration and decreasing temperature. In addition CNT/water nanofluids act as non-Newtonian fluid since the dynamic viscosity varies accordingly with a corresponding increase in shear rate.

Acknowledgement

The authors wish to acknowledge the supports from NRF of South Africa and the College of Agriculture, Engineering and Science of the University of KwaZulu-Natal, South Africa.

References

[1] M. R. Kamesh and D. Madhu, "Effect of Nanoparticles on the Emissions of a CI Engine," *International Journal of Renewable Energy Research,* Journal vol. 7, no. 2, 2017.

[2] I. Carlucci, G. Mutani, and M. Martino, "Assessment of potential energy producible from agricultural biomass in the municipalities of the Novara plain," in *Renewable Energy Research and Applications (ICRERA), 2015 International Conference on*, 2015, pp. 1394-1398: IEEE.

[3] Y. İ. Tosun, "5MW hybrid power generation with agriculture and forestry biomass waste co-incineration in stoker and subsequent solar panel (CSP) ORC station," in *Renewable Energy Research and Applications (ICRERA), 2015 International Conference on*, 2015, pp. 583-589: IEEE.

[4] Y. İ. Tosun, "The proposed design of co-combustion stoker for Şırnak agricultural biomass waste and Şırnak asphaltite in 35MW electricty production," in *Renewable Energy Research and Applications (ICRERA), 2015 International Conference on*, 2015, pp. 358-363: IEEE.

[5] O. Nakagoe, Y. Furukawa, S. Tanabe, Y. Sugai, and R. Narikiyo, "Hydrogen production from steam reforming of woody biomass with cobalt catalyst," in *Renewable Energy Research and Applications (ICRERA), 2012 International Conference on*, 2012, pp. 1-4: IEEE.

[6] S. Mohapatra and K. Gadgil, "Biomass: The Ultimate Source of Bio Energy," *International Journal of Renewable Energy Research,* vol. 3, no. 1, p. 4, 2013 2013.

[7] M. Ahiduzzaman and A. S. Islam, "Assessment of Rice Husk Briquette Fuel Use as an Alternative Source of Wood Fuel," *international Journal of Renewable Energy Research,* vol. 6, no. 4, 2016.

[8] D. D. Guta, "Assessment of biomass fuel resource potential and utilization in Ethiopia: sourcing strategies for renewable energies," *International Journal of Renewable Energy Research (IJRER),* vol. 2, no. 1, pp. 131-139, 2012.

[9] G. Di Giacomo and L. Taglieri, "Development and evaluation of a new advanced solid bio-fuel and related production process," *International Journal of Renewable Energy Research (IJRER),* vol. 3, no. 2, pp. 255-260, 2013.

[10] K. A. Fayemiwo, S. H. Awojide, and C. A. Beckley, "Potential Use of Jatropha Curcas Stem for Ethanol Production," *International Journal of Renewable Energy Research (IJRER),* vol. 3, no. 1, pp. 68-72, 2013.

[11] S. K. Das, S. U. Choi, W. Yu, and T. Pradeep, *Nanofluids: science and technology*. John Wiley & Sons, 2007.

[12] X. Qi, C. Qin, W. Zhong, C. Au, X. Ye, and Y. Du, "Large-Scale Synthesis of Carbon Nanomaterials by Catalytic Chemical Vapor Deposition: A Review of the Effects of Synthesis Parameters and Magnetic Properties," *Materials,* vol. 3, no. 8, pp. 4142-4174, 2010.

[13] S. U. S. Choi and J. A. Eastman, *Enhancing thermal conductivity of fluids with nanoparticles*. 1995, p. Medium: ED; Size: 8 p.

[14] S.-S. Choi, "Nanofluid technology: current status and future research," Argonne National Lab., IL (US)1998.

[15] S. Sharma, P. Ranjan, S. Das, S. Gupta, R. Bhati, and A. Majumdar, "Synthesis of Carbon Nanotube Using Olive Oil and its Application in Dye Sensitized Solar Cell," *Intenational Journal*

of Renewable Energy Research, vol. 2, no. 2, 2012.

[16] P. Kim, L. Shi, A. Majumdar, and P. L. McEuen, "Thermal Transport Measurements of Individual Multiwalled Nanotubes," *Physical Review Letters,* vol. 87, no. 21, 2001.

[17] S.-G. Jeong, O. Chung, S. Yu, S. Kim, and S. Kim, "Improvement of the thermal properties of Bio-based PCM using exfoliated graphite nanoplatelets," *Solar Energy Materials and Solar Cells,* vol. 117, pp. 87-92, 2013.

[18] M. R. Snowdon, A. K. Mohanty, and M. Misra, "A Study of Carbonized Lignin as an Alternative to Carbon Black," *ACS Sustainable Chemistry & Engineering,* vol. 2, no. 5, pp. 1257-1263, 2014.

[19] J. Prasek *et al.*, "Methods for carbon nanotubes synthesis—review," *Journal of Materials Chemistry,* vol. 21, no. 40, pp. 15872-15884, 2011.

[20] H. Dai, "Carbon nanotubes: synthesis, integration, and properties," *Accounts of chemical research,* vol. 35, no. 12, pp. 1035-1044, 2002.

[21] H. Li, X. He, Y. Liu, H. Yu, Z. Kang, and S.-T. Lee, "Synthesis of fluorescent carbon nanoparticles directly from active carbon via a one-step ultrasonic treatment," *Materials Research Bulletin,* vol. 46, no. 1, pp. 147-151, 2011.

[22] B. Zhang, C. y. Liu, and Y. Liu, "A Novel One-Step Approach to Synthesize Fluorescent Carbon Nanoparticles," *European Journal of Inorganic Chemistry,* vol. 2010, no. 28, pp. 4411-4414, 2010.

[23] B. De and N. Karak, "A green and facile approach for the synthesis of water soluble fluorescent carbon dots from banana juice," *Rsc Advances,* vol. 3, no. 22, pp. 8286-8290, 2013.

[24] S. Manafi, M. Amin, M. Rahimipour, E. Salahi, and A. Kazemzadeh, "High-yield synthesis of multiwalled carbon nanotube by mechanothermal method," *Nanoscale research letters,* vol. 4, no. 4, pp. 296-302, 2009.

[25] A. Szabó, C. Perri, A. Csató, G. Giordano, D. Vuono, and J. B. Nagy, "Synthesis methods of carbon nanotubes and related materials," *Materials,* vol. 3, no. 5, pp. 3092-3140, 2010.

[26] Ö. Güler and E. Evin, "Carbon nanotubes formation by short-time ball milling and annealing of graphite," *Optoelectronics And Advanced Materials,* vol. 6, no. 1-2, pp. 183-187, 2012.

[27] M. J. Rak, T. Friscic, and A. Moores, "Mechanochemical synthesis of Au, Pd, Ru and Re nanoparticles with lignin as a bio-based reducing agent and stabilizing matrix," *Faraday Discuss,* vol. 170, pp. 155-67, 2014.

[28] K. Xu *et al.*, "Controllable synthesis of single-and double-walled carbon nanotubes from petroleum coke and their application to solar cells," *Carbon,* vol. 68, pp. 511-519, 2014.

[29] O. V. Kharissova, H. V. Dias, B. I. Kharisov, B. O. Perez, and V. M. Perez, "The greener synthesis of nanoparticles," *Trends Biotechnol,* vol. 31, no. 4, pp. 240-8, Apr 2013.

[30] J. Qu, C. Luo, Q. Cong, and X. Yuan, "Carbon nanotubes and Cu–Zn nanoparticles synthesis using hyperaccumulator plants," *Environmental chemistry letters,* vol. 10, no. 2, pp. 153-158, 2012.

[31] J. Qu, C. Luo, and X. Yuan, "Synthesis of hybrid carbon nanotubes using Brassica juncea L. application to photodegradation of bisphenol A," *Environmental Science and Pollution Research,* vol. 20, no. 6, pp. 3688-3695, 2013.

[32] J. Zhu, J. Jia, F. L. Kwong, D. H. L. Ng, and S. C. Tjong, "Synthesis of multiwalled carbon nanotubes from bamboo charcoal and the roles of minerals on their growth," *biomass and bioenergy,* vol. 36, pp. 12-19, 2012.

[33] A. K. Mittal, Y. Chisti, and U. C. Banerjee, "Synthesis of metallic nanoparticles using plant extracts," *Biotechnol Adv,* vol. 31, no. 2, pp. 346-56, Mar-Apr 2013.

[34] R. Tsao, "Chemistry and biochemistry of dietary polyphenols," *Nutrients,* vol. 2, no. 12, pp. 1231-46, Dec 2010.

[35] X. He, H. Li, Y. Liu, H. Huang, Z. Kang, and S.-T. Lee, "Water soluble carbon nanoparticles: hydrothermal synthesis and excellent photoluminescence properties," *Colloids and Surfaces B: Biointerfaces,* vol. 87, no. 2, pp. 326-332, 2011.

[36] P. Gonugunta, S. Vivekanandhan, A. K. Mohanty, and M. Misra, "A study on synthesis and characterization of biobased carbon nanoparticles from lignin," *World Journal of Nano Science and Engineering,* vol. 2, no. 03, p. 148, 2012.

[37] V. Roshni and D. Ottoor, "Synthesis of carbon nanoparticles using one step green approach and their application as mercuric ion sensor," *Journal of Luminescence,* vol. 161, pp. 117-122, 2015.

[38] T. A. Hassan, V. K. Rangari, V. Fallon, Y. Farooq, and S. Jeelani, "Mechanochemical and sonochemical synthesis of bio-based nanoparticles," in *Proceedings of the Nanotechnology Conference,* 2010, pp. 278-281.

[39] T. S. Syamsudin, E. M. Alamsyah, and B. S. Purwasasmita, "Synthesis of Bio-based Nanomaterial from Surian (Toona sinensis Roem) Wood Bark Using Conventional Balls Milling Method and its Characterization," *Journal of Biological Sciences,* vol. 14, no. 3, p. 204, 2014.

[40] Z. Niu and Y. Fang, "Effects of synthesis time for synthesizing single-walled carbon nanotubes over Mo–Fe–MgO catalyst and suggested growth mechanism," *Journal of crystal growth,* vol. 297, no. 1, pp. 228-233, 2006.

[41] S. D. Mhlanga, K. C. Mondal, R. Carter, M. J. Witcomb, and N. J. Coville, "The effect of

synthesis parameters on the catalytic synthesis of multiwalled carbon nanotubes using Fe-Co/CaCO3 catalysts," *South African Journal of Chemistry,* vol. 62, pp. 67-76, 2009.

[42] W. Zhao, H. S. Kim, H. T. Kim, J. Gong, and I. J. Kim, "Synthesis and Growth of Multi-Walled Carbon Nnotubes(MWNTs) by CCDV Using Fe-Supported Zeolite Templates," *Journal of Ceramic Processing Research,* vol. 12, no. 4, pp. 392-397, 2011.

[43] E. Dündar-Tekkaya and N. Karatepe, "Effect of reaction time, weight ratio, and type of catalyst on the yield of single-wall carbon nanotubes synthesized by chemical vapor deposition of acetylene," *Fullerenes, Nanotubes and Carbon Nanostructures,* vol. 23, no. 6, pp. 535-541, 2015.

[44] S. M. Toussi, A. Fakhru'l-Razi, and A. Suraya, "Optimization of Synthesis Condition for Carbon Nanotubes by Catalytic Chemical Vapor Deposition (CCVD)," in *IOP Conference Series: Materials Science and Engineering*, 2011, vol. 17, no. 1, p. 012003: IOP Publishing.

[45] D. Lopez, I. Abe, and I. Pereyra, "Temperature effect on the synthesis of carbon nanotubes and core–shell Ni nanoparticle by thermal CVD," *Diamond and Related Materials,* vol. 52, pp. 59-65, 2015.

[46] M. Shamsudin, N. Asli, S. Abdullah, S. Yahya, and M. Rusop, "Effect of synthesis temperature on the growth iron-filled carbon nanotubes as evidenced by structural, micro-raman, and thermogravimetric analyses," *Advances in Condensed Matter Physics,* vol. 2012, 2012.

[47] Y. Jiang and C. Lan, "Low temperature synthesis of multiwall carbon nanotubes from carbonaceous solid prepared by sol-gel autocombustion," *Materials Letters,* 2015.

[48] M. Kumar, "Carbon Nanotube Synthesis and Growth Mechanism " in *Carbon Nanotubes - Synthesis, Characterization, Applications*, D. S. Y. (Ed.), Ed.: InTech, 2011, p. 514.

[49] Š. Kavecký, J. Valúchová, M. Čaplovičová, S. Heissler, P. Šajgalík, and M. Janek, "Nontronites as catalyst for synthesis of carbon nanotubes by catalytic chemical vapor deposition," *Applied Clay Science,* vol. 114, pp. 170-178, 2015.

[50] Y. Li, J. Liu, Y. Wang, and Z. L. Wang, "Preparation of monodispersed Fe-Mo nanoparticles as the catalyst for CVD synthesis of carbon nanotubes," *Chemistry of Materials,* vol. 13, no. 3, pp. 1008-1014, 2001.

[51] I. Abdullahi, N. Sakulchaicharoen, and J. E. Herrera, "Selective synthesis of single-walled carbon nanotubes on Fe–MgO catalyst by chemical vapor deposition of methane," *Diamond and Related Materials,* vol. 41, pp. 84-93, 2014.

[52] G. Allaedini, S. M. Tasirin, and P. Aminayi, "Synthesis of CNTs via chemical vapor deposition of carbon dioxide as a carbon source in the presence of NiMgO," *Journal of Alloys and Compounds,* vol. 647, pp. 809-814, 2015.

[53] W.-W. Liu, A. Aziz, S.-P. Chai, A. R. Mohamed, and U. Hashim, "Synthesis of single-walled carbon nanotubes: Effects of active metals, catalyst supports, and metal loading percentage," *Journal of Nanomaterials,* vol. 2013, p. 63, 2013.

[54] Y. Sun, T. Nakayama, and H. Yoshikawa, "Synthesis of uniform single-wall carbon nanotubes using Mn 12 clusters as the catalyst precursor," *Diamond and Related Materials,* vol. 56, pp. 42-46, 2015.

[55] H. Cheng *et al.*, "Large-scale and low-cost synthesis of single-walled carbon nanotubes by the catalytic pyrolysis of hydrocarbons," *Applied Physics Letters,* vol. 72, no. 25, pp. 3282-3284, 1998.

[56] M. Kumar and Y. Ando, "Chemical vapor deposition of carbon nanotubes: a review on growth mechanism and mass production," *Journal of nanoscience and nanotechnology,* vol. 10, no. 6, pp. 3739-3758, 2010.

[57] A. L. M. Reddy, M. Shaijumon, and S. Ramaprabhu, "Alloy hydride catalyst route for the synthesis of single-walled carbon nanotubes, multi-walled carbon nanotubes and magnetic metal-filled multi-walled carbon nanotubes," *Nanotechnology,* vol. 17, no. 21, p. 5299, 2006.

[58] P. M. Parthangal, R. E. Cavicchi, and M. R. Zachariah, "A generic process of growing aligned carbon nanotube arrays on metals and metal alloys," *Nanotechnology,* vol. 18, no. 18, p. 185605, 2007.

[59] M. Shaijumon, A. L. M. Reddy, and S. Ramaprabhu, "Single step process for the synthesis of carbon nanotubes and metal/alloy-filled multiwalled carbon nanotubes," *Nanoscale Research Letters,* vol. 2, no. 2, pp. 75-80, 2007.

[60] F. Xu, H. Zhao, and D. T. Stephen, "Carbon nanotube synthesis on catalytic metal alloys in methane/air counterflow diffusion flames," *Proceedings of the Combustion Institute,* vol. 31, no. 2, pp. 1839-1847, 2007.

[61] C. L. Cheung, A. Kurtz, H. Park, and C. M. Lieber, "Diameter-controlled synthesis of carbon nanotubes," *The Journal of Physical Chemistry B,* vol. 106, no. 10, pp. 2429-2433, 2002.

[62] X.-Q. Wang and A. S. Mujumdar, "Heat transfer characteristics of nanofluids: a review," *International Journal of Thermal Sciences,* vol. 46, no. 1, pp. 1-19, 2007.

[63] V. Khullar and H. Tyagi, "A study on environmental impact of nanofluid-based concentrating solar water heating system," *International Journal of Environmental Studies,* vol. 69, no. 2, pp. 220-232, 2012.

[64] M.-S. Liu, M. Ching-Cheng Lin, I. T. Huang, and C.-C. Wang, "Enhancement of thermal conductivity with carbon nanotube for nanofluids," *International Communications in*

Heat and Mass Transfer, vol. 32, no. 9, pp. 1202-1210, 2005.

[65] Y. Ding, H. Alias, D. Wen, and R. A. Williams, "Heat transfer of aqueous suspensions of carbon nanotubes (CNT nanofluids)," *International Journal of Heat and Mass Transfer,* vol. 49, no. 1-2, pp. 240-250, 2006.

[66] M. Xing, J. Yu, and R. Wang, "Experimental study on the thermal conductivity enhancement of water based nanofluids using different types of carbon nanotubes," *International Journal of Heat and Mass Transfer,* vol. 88, pp. 609-616, 2015.

[67] T. Maré, S. Halelfadl, S. Van Vaerenbergh, and P. Estellé, "Unexpected sharp peak in thermal conductivity of carbon nanotubes water-based nanofluids," *International Communications in Heat and Mass Transfer,* vol. 66, pp. 80-83, 2015.

[68] A. M. A. Soliman, A. K. Abdel-Rahman, S. H. Taher, and S. Ookawara, "Performance Enhancement of Vapor Compression Cycle Using Nanomaterial," presented at the 4th International Conference on Renewable Energy research and Applications, Patermo, Italy, 22-25 November 2015, 2015.

[69] T. Y. Choi, D. Poulikakos, J. Tharian, and U. Sennhauser, "Measurement of thermal conductivity of individual multiwalled carbon nanotubes by the 3-ω method," *Applied Physics Letters,* vol. 87, no. 1, p. 013108, 2005.

[70] A. E. Aliev, M. H. Lima, E. M. Silverman, and R. H. Baughman, "Thermal conductivity of multi-walled carbon nanotube sheets: radiation losses and quenching of phonon modes," *Nanotechnology,* vol. 21, no. 3, p. 035709, 2010.

[71] L. Lu, W. Yi, and D. L. Zhang, "3ω method for specific heat and thermal conductivity measurements," *Review of Scientific Instruments,* vol. 72, no. 7, p. 2996, 2001.

[72] S. K. Das, S. U. Choi, and H. E. Patel, "Heat transfer in nanofluids—a review," *Heat transfer engineering,* vol. 27, no. 10, pp. 3-19, 2006.

[73] S. Vollebregt, S. Banerjee, K. Beenakker, and R. Ishihara, "Thermal conductivity of low temperature grown vertical carbon nanotube bundles measured using the three-ω method," *Applied Physics Letters,* vol. 102, no. 19, p. 191909, 2013.

[74] H. Xie, A. Cai, and X. Wang, "Thermal diffusivity and conductivity of multiwalled carbon nanotube arrays," *Physics Letters A,* vol. 369, no. 1-2, pp. 120-123, 2007.

[75] D. J. Yang *et al.*, "Thermal conductivity of multiwalled carbon nanotubes," *Physical Review B,* vol. 66, no. 16, 2002.

[76] M. K. Samani, N. Khosravian, G. C. K. Chen, M. Shakerzadeh, D. Baillargeat, and B. K. Tay, "Thermal conductivity of individual multiwalled carbon nanotubes," *International Journal of Thermal Sciences,* vol. 62, pp. 40-43, 2012.

[77] J. Che, T. Cagin, and W. A. Goddard III, "Thermal conductivity of carbon nanotubes," *Nanotechnology,* vol. 11, no. 2, p. 65, 2000.

[78] S. Berber, Y.-K. Kwon, and D. Tománek, "Unusually high thermal conductivity of carbon nanotubes," *Physical review letters,* vol. 84, no. 20, p. 4613, 2000.

[79] J. R. Lukes and H. Zhong, "Thermal Conductivity of Individual Single-Wall Carbon Nanotubes," *Journal of Heat Transfer,* vol. 129, no. 6, p. 705, 2007.

[80] Z. Wang, D. Tang, X. Zheng, W. Zhang, and Y. Zhu, "Length-dependent thermal conductivity of single-wall carbon nanotubes: prediction and measurements," *Nanotechnology,* vol. 18, no. 47, p. 475714, 2007.

[81] J. Hone, M. Whitney, C. Piskoti, and A. Zettl, "Thermal conductivity of single-walled carbon nanotubes," *Physical Review B,* vol. 59, no. 4, p. R2514, 1999.

[82] J. X. Cao, X. H. Yan, Y. Xiao, and J. W. Ding, "Thermal conductivity of zigzag single-walled carbon nanotubes: Role of the umklapp process," *Physical Review B,* vol. 69, no. 7, 2004.

[83] C. Ren, W. Zhang, Z. Xu, Z. Zhu, and P. Huai, "Thermal conductivity of single-walled carbon nanotubes under axial stress," *The Journal of Physical Chemistry C,* vol. 114, no. 13, pp. 5786-5791, 2010.

[84] A. Nasir Imtani, "Thermal conductivity for single-walled carbon nanotubes from Einstein relation in molecular dynamics," *Journal of Physics and Chemistry of Solids,* vol. 74, no. 11, pp. 1599-1603, 2013.

[85] A. V. Savin, Y. S. Kivshar, and B. Hu, "Effect of substrate on thermal conductivity of single-walled carbon nanotubes," *EPL (Europhysics Letters),* vol. 88, no. 2, p. 26004, 2009.

[86] P. Silotia, S. Dabas, A. Saxena, and S.-P. Tewari, "On the Thermal Conductivity of Single-Walled Carbon Nanotube Ropes," *Soft Nanoscience Letters,* vol. 03, no. 01, pp. 7-10, 2013.

[87] A. Duzynska, A. Taube, K. Korona, J. Judek, and M. Zdrojek, "Temperature-dependent thermal properties of single-walled carbon nanotube thin films," *Applied Physics Letters,* vol. 106, no. 18, p. 183108, 2015.

[88] H. Li-Jun, L. Ji, L. Zheng, Q. Cai-Yu, Z. Hai-Qing, and S. Lian-Feng, "Thermal properties of single-walled carbon nanotube crystal," *Chinese Physics B,* vol. 20, no. 9, p. 096101, 2011.

[89] M. A. Osman and D. Srivastava, "Temperature dependence of the thermal conductivity of single-wall carbon nanotubes," *Nanotechnology,* vol. 12, no. 1, p. 21, 2001.

[90] Y. Gu and Y. Chen, "Thermal conductivities of single-walled carbon nanotubes calculated from the complete phonon dispersion relations," *Physical Review B,* vol. 76, no. 13, 2007.

[91] R. Pan, Z. Xu, Z. Zhu, and Z. Wang, "Thermal conductivity of functionalized single-wall carbon nanotubes," *Nanotechnology,* vol. 18, no. 28, p. 285704, 2007.

[92] E. Pop, D. Mann, Q. Wang, K. Goodson, and H. Dai, "Thermal conductance of an individual single-wall carbon nanotube above room temperature," *Nano Lett,* vol. 6, no. 1, pp. 96-100, Jan 2006.

[93] A. Minnich, "Advances in the measurement and computation of thermal phonon transport properties," *Journal of Physics: Condensed Matter,* vol. 27, no. 5, p. 053202, 2015.

[94] Y.-J. Han, "Intrinsic thermal-resistive process of crystals: Umklapp processes at low and high temperatures," *Physical Review B,* vol. 54, no. 13, p. 8977, 1996.

[95] S. Halelfadl, P. Estellé, B. Aladag, N. Doner, and T. Maré, "Viscosity of carbon nanotubes water-based nanofluids: Influence of concentration and temperature," *International Journal of Thermal Sciences,* vol. 71, pp. 111-117, 2013.

[96] B. Jo and D. Banerjee, "Viscosity measurements of multi-walled carbon nanotubes-based high temperature nanofluids," *Materials Letters,* vol. 122, pp. 212-215, 2014.

[97] R. Sadri *et al.*, "An experimental study on thermal conductivity and viscosity of nanofluids containing carbon nanotubes," *Nanoscale Res Lett,* vol. 9, no. 1, p. 151, 2014.

[98] B. Aladag, S. Halelfadl, N. Doner, T. Maré, S. Duret, and P. Estellé, "Experimental investigations of the viscosity of nanofluids at low temperatures," *Applied Energy,* vol. 97, pp. 876-880, 2012.

[99] G. R. Vakili-Nezhaad and A. Dorany, "Investigation of the Effect of Multiwalled Carbon Nanotubes on the Viscosity Index of Lube Oil Cuts," *Chemical Engineering Communications,* vol. 196, no. 9, pp. 997-1007, 2009.

[100] M. Schuller *et al.*, "Molten Salt-Carbon Nanotube Thermal Energy Storage for Concentrating Solar Power Systems Final Report," DOE/GO18154; TRN: US201209%%258 United States10.2172/1036948TRN: US201209%%258Wed Dec 05 11:24:59 EST 2012GFOEnglish, 2012, Available: http://www.osti.gov/scitech//servlets/purl/1036948/.

[101] S. Halelfadl, T. Maré, and P. Estellé, "Efficiency of carbon nanotubes water based nanofluids as coolants," *Experimental Thermal and Fluid Science,* vol. 53, pp. 104-110, 2014.