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VOLUME FRACTION EFFECT OF CALCINED EGGSHELL AND TITANIUM OXIDE HYBRID NANO PARTICLES ON VISCOSITY AND THERMAL CONDUCTIVITY OF AUTOMOBILE COOLANT

F. O. Oshomogho*[1] and E. A. Oyedoh[1]

[1] Chemical Engineering Department, University of Benin, PMB 1154, Benin City. Nigeria.

corresponding_fred.oshomogho@uniben.edu

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Abstract— This study seeks to investigate the effects of the addition of nanoparticles on the viscosity and thermal conductivity of ethylene glycol-based automobile engine coolants. Nanoparticles were prepared from crushed, calcined eggshells and titanium oxide blends. Formulation of nanofluid was conducted by volume fraction addition of nanoparticles from 0.001ø to 0.050ø to ethylene glycol. The fluid was completely homogenized with a magnetic stirrer and ultrasonic sonicator for particle stability. Viscosities and thermal conductivities were determined at temperatures between 30 to 70°C using digital rotary viscometers equip with a thermocouple. Results obtained

Ethylene Glycol	revealed that a higher volume fraction of the process fluid resulted in higher heat transfer coefficients. Thermal conductivity of the base fluid was thus observed to depend on the volume fraction of nanoparticles and the increase with the increase in volume fraction is because of the high heat thermal conductivities of the elemental content of the nanoparticle. Therefore, thermal conductivity enhancement in nanofluids is essentially dependent on the nature of the nanoparticles.

I. Introduction

Most engine coolants contain ethylene glycol and other chemical components added to distilled water [1]. Nanofluids which are produced by suspending nanoparticles in coolants have greatly enhanced the cooling performance of most engine coolants [2]. Nanoparticles have provided some encouraging results in applications such as automobile coolants. It is now known that thermal conductivity enhancement of nanofluids depends on several factors, namely particle size, concentration, nature of base fluids, pH value of the nanofluids, fluid temperature and the effect of clustering of nanoparticles [2]. Water is the most used coolant. The low cost and high heat capacity make very suitable heat-transfer medium [3]. Corrosion inhibitors and antifreeze are its main additives. Today, base fluids including water, ethylene glycol, and oil are combined with different types of metallic nanoparticles to improve the thermal performance of cooling systems. The metallic compounds, such as CuO, SiO_2, WO_3, TiO_2, ZrO_2, ZnO, Fe_3O_4, Al_2O_3, and so on, as well as the metallic nanoparticles, such as Cu, Fe, Au, Ag, etc., are frequently used with base fluids [1].

Antifreeze is added when the water-based coolant has to withstand very low temperatures that are below 0°C. The convectional force is the important thing that is considered in radiators [4]. Examples of these convectional heat transfer fluids are nanofluid, water, glycerol, Ethylene Glycol and minerals oil [1]. These base fluids have been used mainly in automotive radiators and these fluids recently were confirmed to have very low thermal conductivities. According to Naraki et al. [5], the experiment which was conducted under laminar flow in a car radiator revealed that the overall heat transfer coefficient of nanofluid with a high volume fraction of nanoparticles was more than the base fluid alone without the addition of nanoparticles which also agrees with the work done to study forced convection heat transfer of Fe_2O_3 and CuO nanofluids in car radiator by Rafi et al. [6]. Therefore, One of the strategies to increase the heat transfer in car radiators is by using nanofluid because it is an innovation that can be obtained by dispersing nanoparticles on the base fluids [7]. This is because the thermal conductivity of the particles is higher than standard or base liquids [8]. This study produces nanoparticles from calcined waste chicken eggshell and titanium oxide blend to be used as an additive to ethylene glycol-based coolants to enhance the viscosity and thermal conductivity of the nanofluid. The use of nanoparticles derived from waste bio-material will be beneficial as engine coolants due to their cost effectiveness as most commercial nanoparticles are expensive.

II. Materials and Methodology

Waste eggshells used in this study were locally obtained from an eatery. Ethylene glycol and titanium dioxide were purchased as pure and analytical grade produced by Loba Chemie, India. The major equipment used was a Rotary viscometer, Brookfield NDJ-5S, England. Ultrasonic Sonicator Bath, Bandelin SonoRex, RK 100 H, Berlin, Germany. Constant temperature magnetic stirrer; Jinotech MS300, Guangdong, China. Thermostatic water bath, B-Scientific HH-4, England.

A. Preparation and Characterization of Calcined Eggshell and Titanium oxide Blend

Eggshells were washed with a large amount of water to remove unwanted materials and then sundried for several hours to reduce moisture content. Nanoparticles were prepared as shown in Figure 1. Sundried shells were subjected to further drying in a constant temperature thermostatic air-dry oven at 110ºC to completely remove residual moisture content. Dried shells were ground into fine particles with the aid of a mechanical grinder and sieved through a 50µm mesh. The finely powdered shells were put into 50ml crucibles and calcined in a muffle furnace at 900ºC with a heating rate of 10°C/min for 6hrs after which it was allowed to cool to room temperature in a desiccator. Calcined eggshell was dispersed in adequate amount of deionized water and stirred for 60minutes with a magnetic stirrer to induce a colloidal suspension of the nano-sized particles. The solution was filtered through a filter paper of 0.45µm pore diameter to separate the nanoparticles. The filtrate was centrifuged for 30 minutes and the solid was collected and oven dried at 105ºC for 4 hours to obtain an ultrafine particle.

Figure 1: Nanoparticles production process

B. Preparation of Nanofluid

Exactly 50g of the cooled calcined eggshell was added to TiO_2 in a ratio of 10:1. This was dissolved in 50ml distilled and deionized water and was thoroughly mixed to form a paste, dried in an oven at 110ºC and again subjected to thermal treatment in a furnace at 600ºC for 3hours after which it was cooled in a desiccator. The calcined eggshells and TiO_2 blend (CES/TiO_2) nanoparticles of volume fraction between 0.001φ to 0.050φ were estimated from Equation (1) according to Kole and Dey [9]. Volume fractions of the sample were calculated using the weight of the dry powder from the true density and the total volume of suspension.

Nanofluid was prepared by dispersing an appropriate quantity of nanoparticles into 100g of base fluid (ethylene glycol). The mixture was thoroughly emulsified with the aid of a magnetic stirrer at 1,500rpm stirring speed for 2 hours to obtain a stable heterogeneous mixture. The homogenization was further enhanced by treating in a Sonicator for 2 hours to enhance the stability of the nanoparticles in the base fluid. The nanofluid was then monitored for several hours to ensure complete dispersion and stability. Thermal conductivity and viscosity tests were therefore carried out immediately.

Volumetric fraction;

$$\varphi \times 100 = \left[\frac{\frac{W_P}{\rho_P}}{\frac{W_P}{\rho_P}+\frac{W_F}{\rho_F}}\right] \tag{1}$$

where:

W_P = weight of nanoparticle,

ρ_P = density of nanoparticle,

W_F = weight of base fluid,

ρ_F = density of base fluid

C. Thermal Conductivity Measurement

Thermal conductivity was experimentally determined in conformity with ASTM D5334. The apparatus consists of a handheld thermocouple with a sensor for measuring the thermal conductivity of the fluid in a controlled constant temperature environment using a water bath within temperature accuracy of 0.1°C. A 50ml bottle containing 30ml of nanofluid sample related to a temperature sensor inserted through the orifice at the top of the bottle cover which is designed for perfect fit by a needle. The sample with the thermocouple was lowered into the water bath thereby taking sets of readings at intervals of 15mins for each sample and the average value considered at that temperature for a temperature range of 30°C to 70°C.

D. Viscosity Measurement

Viscosity of base fluids was easily measured with the aid of Brookfield Digital viscometer attached to a thermostatic water-bath which is capable of measuring viscosity in the range of 1 to 6,000,000 mPa.s. A Rheocal programme was used in acquiring the data at specified temperature and torque for each measurement. Sample to be evaluated (16ml) is placed in a cylinder jacket and the entire unit is attached to the digital viscometer with constant heating and a sensor to determine the specified test temperature. A minimum of 3 experimental trials at each test temperature were taken with an average value considered for further application.

III. Results and Discussion

A. Results of Nanoparticles Analysis

The characteristics of the nanoparticle blend are shown in Table 1 as results. The particles sizes of CES/ TiO_2 blend were 450nm, whereby the pure TiO_2 particle sizes were about 250nm. The density of the blend was 3.75g/cm^3. Because heat transmission is increased by the more active Brownian motion and heat transfer of small particles compared to those of large particles, smaller particles have higher surface area per unit volume than larger ones. As a result, the use of nanoparticles increases thermal conductivity and speeds up heat transfer.

Results obtained from nanoparticles analysis with a Quantachrome NovaWin BET Data acquisition and reduction instrument version 11.03 using the BJH/DH method of nitrogen adsorption are shown in Figure 2. Surface area, pore volume and pore diameter were 247.474m^2/g, 0.122cc/g and 2.138nm respectively.

Table 1: Properties of nanoparticles and nanofluid

Property	CES/TiO_2 Blend
Particle size (nm)	<450
Specific surface area (m^2/g)	247.474
Density (g/cm^3)	3.75

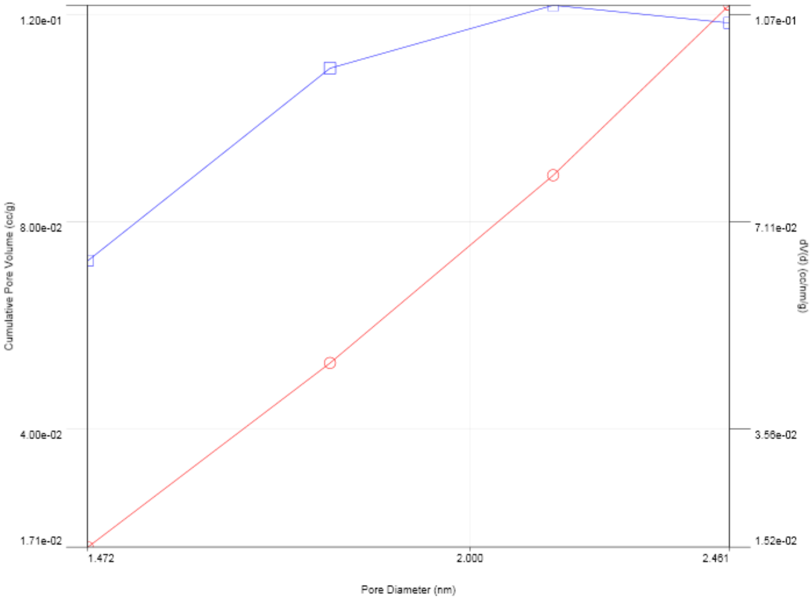

Figure 2: BJH Adsorption of nitrogen

Elemental Composition of Nanoparticles

The major elements contained in the synthesized nanoparticles were determined by Energy Dispersive Spectroscopy X-ray Fluorescence (EDXRF) with an ARL® 9800 XP spectrometer. The spectrum (Figure 3) revealed a concentration 89.516wt% Ca as the most predominant element which is attributed to the high calcium content in eggshells [10, 11]. A concentration of 5.657wt% Ti was obtained as a result of the blend with titanium dioxide. This combination was formulated to increase the thermal effectiveness of the nanoparticles with the high thermal conductivity of 200

W/(mK) Ca and 17 (W/mK) Ti [12, 13]. Magnesium (Mg), silicon (Si), aluminum (Al) and potassium were also present at very low concentrations of 1.27wt%, 0.3152wt%, 0.434wt% and 0.2634% respectively. The main component in powdered chicken eggshell is calcium carbonate (CaCO3), which makes up roughly 90% of it.

Surface Morphology of Nanoparticles

Morphology and microanalysis of the nanoparticles were determined using an ultra-high resolution field emission scanning electron microscope (UHR-FEGSEM). Particle images were obtained with a secondary electron detector. The SEM micrographs of the powder nanoparticle sample are shown in Figure 4.

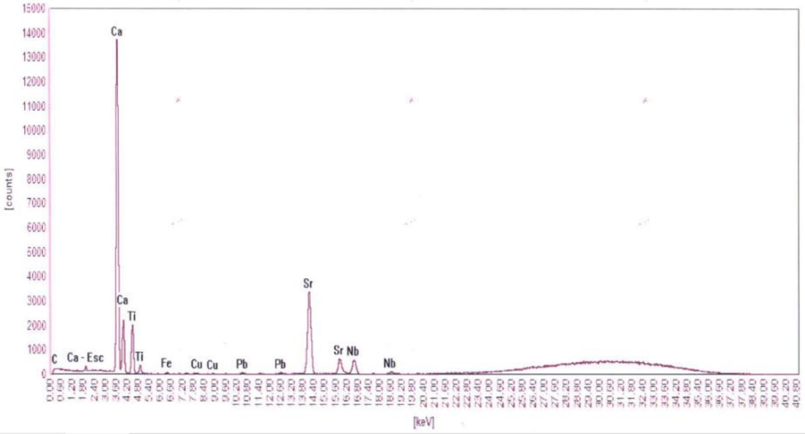

Figure 3: EDXRF Spectrum of CES/TiO_2 nanoparticle

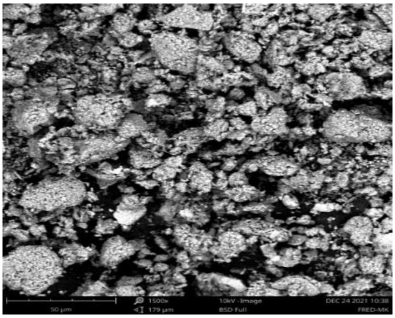

Figure 4: Micrograph of CES/TiO_2 nanoparticles

B. Properties of Nanofluid

The thermo-physical properties of the nanofluid were used for estimation of the heat transfer coefficient. The properties of the nanofluids are expressed in percentage of volume concentration, while the loading analysis was obtained in weight per cent (wt%). The density and specific heat of nanofluid were estimated using solid–liquid mixture equations (Equations 2 and 3). The dynamic viscosity and thermal conductivity of ethylene glycol and CES/TiO_2 based nanofluid were measured for each concentration using a rotary viscometer and an experimental set-up for the determination of thermal.

Density and Viscosity of Nanofluid

The density of the CES/TiO_2 based nanofluid was affected by the volume fraction of the nanoparticle and thus has influenced the heat transfer characteristics of the fluid [14] . Though, not much literature report was found on the effectiveness of volume fraction of nanoparticles on the density of nanofluids. The reported density of the nanofluid in this study was estimated according to Pak and Cho [15] from Equation 2 by taking into account the density and volume fraction of base fluid and nanoparticles.

$$\rho_{nf} = \o\rho_s + (1 - \o)\rho_f \qquad (2)$$

As shown in Figure 5, there is a corresponding increase in density from 1.006033g/cm^3 to 1.076245g/cm^3 as volume fraction increases from 0.001**ø** to 0.05**ø** respectively at 30°C.

In the absence of any prior data on the viscosity of the present nanofluids (ethylene glycol and CES/TiO_2 mixture), it is important to ascertain whether they display Newtonian or non-Newtonian behaviour as a function of particle loading and temperature. Figure 6 shows the effects of volume fractions on the viscosities of nanofluids. It may be noted that an increase in volume fractions increases the viscosity of the nanofluids.

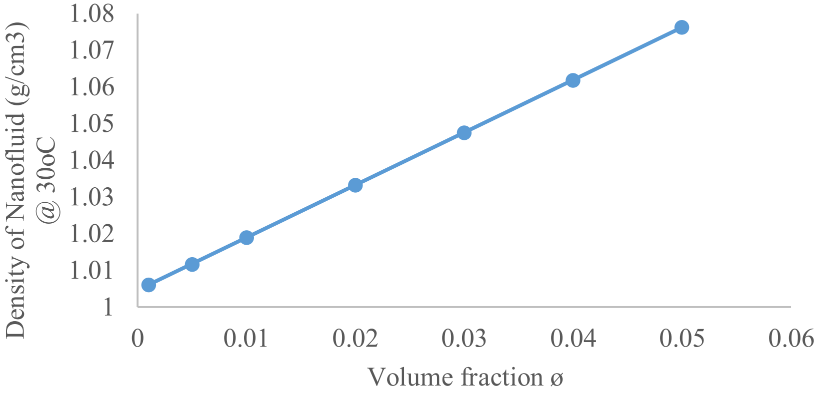

Figure 5: Density of nanofluid at 30°C

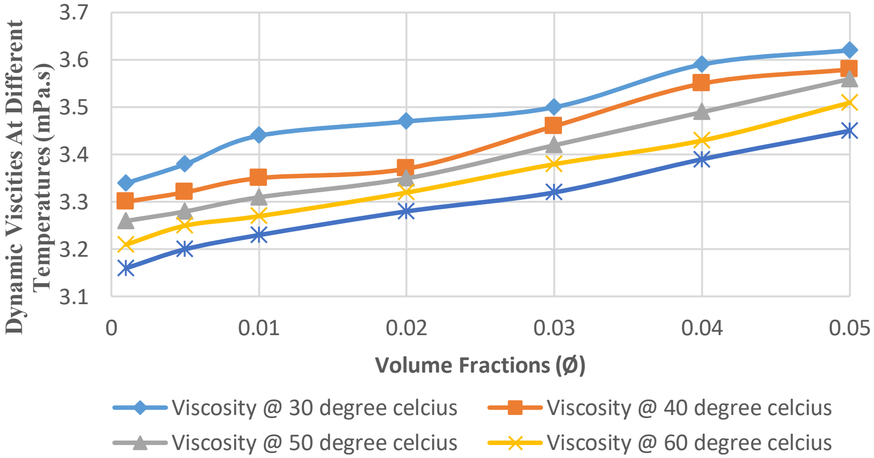

Figure 6: Dynamic viscosities of nanofluid (mPa.s)

Figure 7 showed the low loading of CES/TiO_2, the liquid reveals Newtonian behaviour only at higher temperatures, while nanofluids with higher CES/TiO_2 loading display non-Newtonian characteristics over the measured temperature range. At room temperature (30°C), the shear stress increases linearly with the shear strain rate for low loading of CES/TiO_2 but this was not the case at a higher temperatures of about 70°C [9].

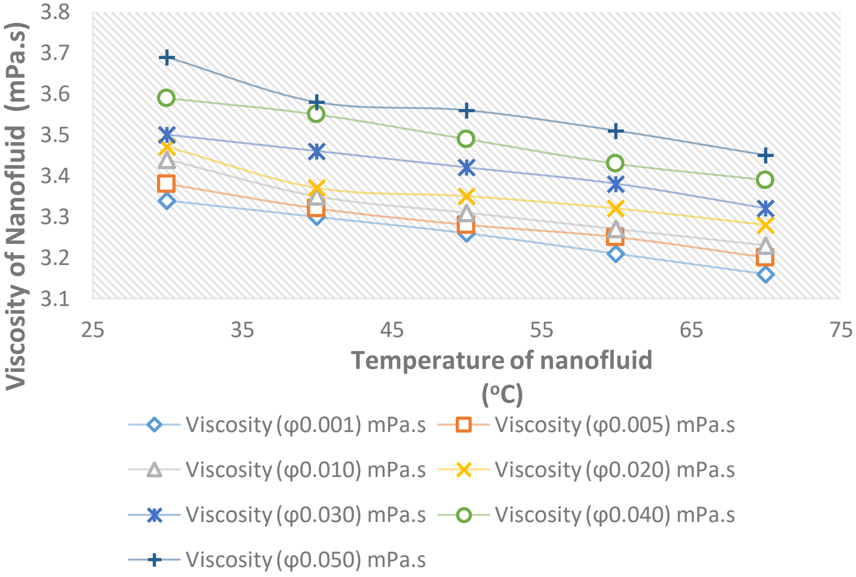

Figure 7: Effects of temperature on viscosity and volume fraction of nanofluid

Specific Heat Capacity of Nanofluid

Nanoparticles of metal oxides enhance the heat transfer coefficient by an increase in the heat capacity as well as the thermal conductivity of the overall system, and the movement of the nanoparticles relative to the streamlines [16]. Figure 8 showed that higher volume fractions of the process fluid resulted in higher heat transfer coefficients. As the process fluid begins to be heated at the entrance of the exchanger, the fluid viscosity decreases. The specific heat of a nanofluid which was obtained from Equation (3) according to Pak and Cho [15] was used to estimate the specific heat capacity of nanofluids [17].

$$C_{p,nf}\rho_{nf} = (1-\emptyset)Cp_f\rho_{bf} + \emptyset\rho_{np}Cp_{np} \qquad (3)$$

where:

C_p = specific heat,

$\emptyset$ = volume fraction,

ρ = density,

subscripts *np*, *nf*, and *bf* refer to a nanoparticle, nanofluid, and base fluid, respectively.

The specific heat capacity of ethylene glycol $(Cp)_{bf}$ 2.433J/g°C was used to validate this procedure [18]. The specific heat capacity of nanoparticles was estimated as $(Cp)_{np}$ 1.983J/g°C according to Fono-Tamo and Koya [19]. The estimation was done in comparison with a theoretical model on the assumption of thermal equilibrium between the particles and the surrounding fluid [13].

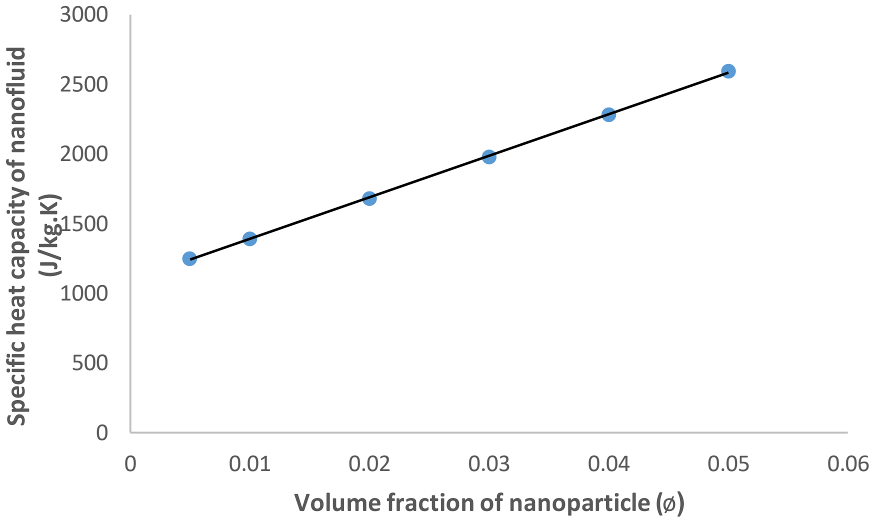

Figure 8: Specific heat capacity of nanofluid

Thermal Conductivity

The thermal conductivity of the calcined eggshell and titanium oxide oxide nanofluid on car engine coolant (k_{nf}) as a function of CES/TiO_2 nanoparticle volume fraction measured at 30°C is shown in Figure 9. The base fluid decreases almost linearly with A CES/TiO_2 nanoparticles' volume fraction. The values of thermal conductivity of nanoparticles were obtained from experimental data using Equation (4). The quantity of heat transferred Q was given by Equation (5).

$$k = \frac{Qd}{\Delta t A \Delta T} \tag{4}$$

$$Q = mC_P\Delta T \tag{5}$$

where:

d = distance between the heat source and nanofluid ($9.37x10^{-3}$m),

m = mass in gram of heat transfer source (500g),

A = heat transfer area (0.07m),

t = time of heat transfer (180seconds),

T = temperature

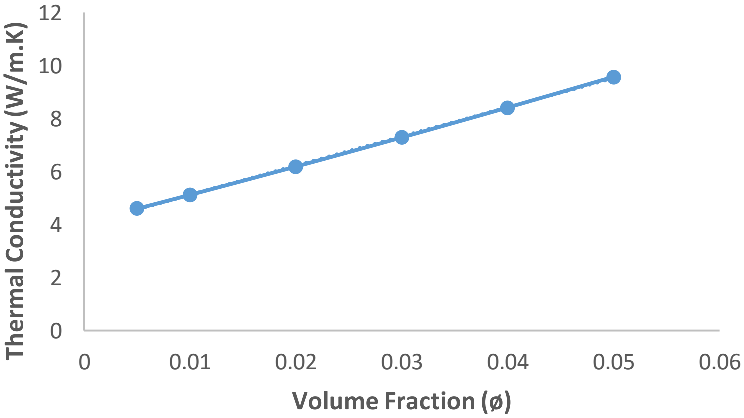

Figure 9: Effect of CES/TiO_2 on Thermal Conductivity of Nanofluid

Figure 9 shows the volume fraction dependence of the thermal conductivity of the nanofluid and the various volume fraction of CES/TiO_2 nanoparticles. The observed volume fractions dependence originates from the dependence on the thermal conductivity of the base fluid. This indicates that the observed increase with the increase in volume fraction is because of the high thermal conductivity of the metal composition of the nanoparticle. These metals enhance the heat transfer in CES/TiO_2 nanoparticles. Therefore, thermal conductivity enhancement in nanofluids is essentially dependent on the composition of the nanoparticles. Similar observations have been reported by Rashmi et al. [21] for water and ethylene glycol-based nanofluids. For temperatures above 40°C, the measured thermal conductivity of the nanofluid with a 0.001ø volume fraction of CES/TiO_2 appears to be slightly higher than that of the base fluid. Therefore, k_{nf} for the nanofluid with 0.001 volume fraction of CES/TiO_2 is essentially the same as that for the base fluid because of the little effect because of the low volume fraction.

IV. Conclusion

Ethylene glycol and CES/TiO_2 based nanofluid automobile coolant have been significantly studied to reveal that thermal conductivity and viscosity are a function of the volume fraction of nanoparticles. The results indicate that the increase of 0.001**ø** to 0.050**ø** volume fraction of calcined eggshell and titanium dioxide blend nanoparticles in ethylene glycol did enhance the thermal conductivity of the fluid because of the high thermal efficiency of the nanoparticle it contained.

The enhancement in thermal conductivity of the nanofluid varies linearly with the volume fraction of the nanoparticles. The thermal conductivity expression well predicts the observed nanoparticle's volume fraction dependence of the thermal conductivity of the present nanofluid. The viscosity of the nanofluids decreases with the CES/TiO_2 volume fraction and decreases with the rise in temperature. Newtonian behaviour was observed for nanofluids with low CES/TiO_2 loading (0.001**ø**) only at higher temperatures, while nanofluids with higher CES/TiO_2 loading displayed non-Newtonian behaviour throughout the measured temperature range.

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