Characteristics of ethylene glycol-Al₂O₃ nanofluids prepared by utilizing Al₂O₃ nanoparticles synthesized from local bauxite

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Abstract. Nanoparticles of Al₂O₃ have been synthesized from local bauxite mineral, and ethylene glycol (EG)-Al₂O₃ nanofluids have been prepared. Powder Al(OOH) was extracted from local bauxite using bayer process, and heated at 600°C for 3 hours to get Al₂O₃ nanoparticles. XRD analyses showed that the Al₂O₃ nanoparticles crystallizes in γ-Al₂O₃ with crystallite size of 4.12 nm. The specific surface area of the Al₂O₃ nanoparticles was 296.72 m²/gr. Viscosity of the EG-Al₂O₃ nanofluids was temperature dependent, and decreased with increasing temperature. The viscosity of the nanofluids increased with the concentration of the Al₂O₃ nanoparticles. Meanwhile, Critical Heat Flux (CHF) enhancement of the nanofluids increased with the concentration of the Al₂O₃ nanoparticles. The largest CHF enhancement was 54% at Al₂O₃ concentration of 0.095 vol %.

1. Introduction
Since term “nanofluid” proposed for the first time by Choi in 1995 [1,2], research on nanofluids intensively carried out worldwide. Nanofluid is a dispersion of nanoparticles with 1-100 nm size in a base fluid forming a stable suspension [1-3]. Some researches on nanofluids especially for heat transfer have been being carried out with the goal of increasing economic value and safety of some systems such as nuclear power, automotive, and electronics, through increasing heat transfer capability of the fluid [4]. Based on literature data, the nanofluids can be prepared by utilizing various nanoparticles and base fluids. One of them that is intensively investigated is ethylene glycol-Al₂O₃ (EG-Al₂O₃) nanofluid. EG-Al₂O₃ nanofluids have been studied by many researchers and some of them are Gallego et al. [5], Hechey et al. [6], Bozorgan [7], Sarafratz et al. [8], Esfe et al. [9], Fal et al. [10], and Yoshino and Torii [11]. In 2013, Yoshino et al. [11] studied thermal conductivity of EG-Al₂O₃ nanofluids by utilizing Al₂O₃ powder with particle size of 31 nm and specific surface area of 55 m²/g. Other than Yoshino, some researchers prepared the nanofluids with relatively large nanoparticles and/or small specific surface area [5,6,8,10]. The synthesis and characterization of nanofluids with small nanoparticles of 4 nm and large surface area of 296.7 m²/g has not been reported so far. In addition, although Yoshino and Torii [11] reported the pH of their nanofluids, however, most of researchers did not report the pH of their nanofluids [5,6,7,9,10]. It is known that the pH is a very important characteristic of the nanofluids. It should be known before measuring other characteristics such as thermal conductivity and critical heat flux (CHF).

Based on the above mentioned background, in this work a study of synthesis of Al₂O₃ nanoparticles and characteristics of ethylene glycol-Al₂O₃ nanofluids was carried out. The pH has a strong relation to the
application of a nanofluid. If the pH is too low the nanofluid will have problem with corrosion. Since the pH of the nanofluids is about 7 (neutral) the corrosion problem diminishes. Therefore, in this study the nanofluids with pH about 7 were prepared. In addition, in order to step up the added value of the local material, also in this study the \( \text{Al}_2\text{O}_3 \) nanoparticles was synthesized from local bauxite. Characteristics of the \( \text{Al}_2\text{O}_3 \) nanoparticles synthesized from local bauxite and those of the nanofluids with pH about 7 especially the viscosity and critical heat flux (CHF) were discussed.

2. Methodology

2.1. Synthesis and Characterization of \( \text{Al}_2\text{O}_3 \) Nanoparticles

Extraction of \( \text{Al(OH)}_3 \) as precursor from local bauxite was done by using Bayer process. The procedure was used in our previous study [12]. The bauxite was mixed with NaOH with 1:1 weight ratio and heated at 175\(^\circ\)C for 3 hours in an autoclave. The heated mixture was placed in a beaker glass. An amount of HCl was added into the mixture until pH = 11. A precipitate formed. The precipitate was washed with aquadest until pH about 7. The washed precipitate was then heated at 600\(^\circ\)C for 3 hours to get \( \text{Al}_2\text{O}_3 \) nanoparticles. The \( \text{Al}_2\text{O}_3 \) nanoparticles was subjected to XRD analyses using a diffractometer from Philips PAN Analytical with \( \text{K}_\alpha \) radiation (\( \lambda=1.5406\text{A} \)) in order to investigate the crystal structure and crystallite size, and to TEM analyses in order to know particle size using a TEM from JEOL. Specific surface area of the nanoparticles was measured using a surface area meter from Quanthachrome.

2.2. Preparation and Characterization of Ethylene Glycol- \( \text{Al}_2\text{O}_3 \) nanofluids

Some nanofluids were prepared utilizing ethylene glycol as base fluid and the \( \text{Al}_2\text{O}_3 \) nanoparticles that already synthesized. The nanofluids were prepared with 4 concentrations of the nanoparticles. The nanoparticles were dispersed into 100 ml ethylene glycol and ultrasonicated using an ultrasonic bath from Branson for 2 hours. After 24 hours from ultrasonication step, the upper part of the nanofluids was extracted and separated from the precipitate. The precipitate was dried and weighed for measuring the concentration of the nanofluids. Visual appearance of the nanofluids was taken using a digital camera. Then, pH of the nanofluids was measured using a pH meter from Mettler Toledo. Meanwhile, zeta potential of the nanofluids was measured using a Zetasizer from Malvren. After that, Critical Heat Flux (CHF) was measured using a laboratory made equipment based on measurement principle found in [13]. Cu wires 0.2 mm in diameter were used for the CHF measurement. The CHF was calculated using equation (1) [13].

\[
\text{CHF} = \frac{IV}{\pi DL}
\]

where, \( I \) is the input current (Amp), \( V \) is the input voltage (Volt), \( D \) is the wire diameter (m), and \( L \) is the wire length (m).

3. Results and Discussions

3.1. Characterization of the \( \text{Al}_2\text{O}_3 \) nanoparticles

Figure 1 reveals the diffraction pattern of the \( \text{Al}_2\text{O}_3 \) nanoparticles synthesized from local bauxite. By comparing to the JCPDS standard no. 29-0063 for \( \gamma\text{-Al}_2\text{O}_3 \), it is clear that the \( \text{Al}_2\text{O}_3 \) nanoparticles crystallizes in \( \gamma\text{-Al}_2\text{O}_3 \) with three strong peaks at \( 2\theta = 38, 46, \) and \( 67^\circ \) which are corresponding to peaks of (311), (400), and (440). From the data of Fig.1, crystallite size was calculated using Debye Scherrer method expressed in equation (2) [14].

\[
d = \frac{0.9\lambda}{\beta\text{Cos}\theta}
\]

where, \( d \) is crystallite size, \( \lambda \) is wavelength (1.5406A), \( \theta \) is diffraction angle, and \( \beta \) is FWHM. From the calculation, it is known that the average crystallite size of the \( \text{Al}_2\text{O}_3 \) nanoparticles is 4.12 nm.
Figure 2 reveals the image of Al$_2$O$_3$ nanoparticles taken using TEM. According to Fig. 2, the Al$_2$O$_3$ nanoparticles form an aggregate. The agglomeration causes the average particle size of the Al$_2$O$_3$ nanoparticles much larger than that measured using the XRD.

The specific surface area of the Al$_2$O$_3$ nanoparticles was determined using the Brunauer Emmet Teller (BET) method. The specific surface area for the Al$_2$O$_3$ nanoparticles was $296.72$ m$^2$/g. This surface area is quite large. It is much larger compared to the surface area of the $\gamma$-Al$_2$O$_3$ found in work of Yoshino and Torii ($55$ m$^2$/g) [4]. If the surface area is converted to particle size by using equation (3) [15] by assuming the nanoparticle is spherical, we get a particle size of $5.12$ nm. This particle size is comparable to crystallite size calculated from data of XRD ($4.12$ nm). This data shows that the particles form an aggregate consisting of small particles ($5.12$ nm) as can be seen in Fig. 2.

$$d = \frac{6000}{A_s \rho} \tag{3}$$

where, $d$ is the particles size, $A_s$ is the specific surface area (m$^2$/g), and $\rho$ is the density of particles in gr/cm$^3$ (In this case is Al$_2$O$_3$ (3.9 gr/cm$^3$)).

3.2. Characterization of Nanofluids

3.2.1. Visual Appearance and Zeta Potential

Figure 3 shows the visual appearance of a nanofluid prepared in this work with concentration of Al$_2$O$_3$ nanoparticles of $0.058$ vol % as an example. The nanofluid is stable. It is shown by a small decrease of the surface height of the nanofluid after 14 days observation. The decrease of the surface height of the nanofluid is about $2\%$ from the initial height. The EG-Al$_2$O$_3$ nanofluid of Sarafraz et al [8] is also stable, however, the pH of their nanofluid is $10.2$, larger than that in this study (about $7$). The best nanofluid of Sarafraz et al. with pH 10.2 is stable until 45 days.

Zeta potential is a measure of the stability of the nanofluid. When a particle gets into a fluid, it will spontaneously have charge and form an electric double layer at the surface of the particle. Zeta potential of the nanofluids was measured using a Zeta sizer from Malvern. Fig. 4 reveals the zeta potential of the nanofluids. As shown in Fig. 3, the nanofluids with different concentrations of the Al$_2$O$_3$ nanoparticles are stable with the zeta potential is larger than $30$ mV. A nanofluid is stable when the zeta potential is larger than $30$ mV or smaller than $-30$ mV. When the zeta potential increases, the repulsion between particles becomes strong and the stability of particles increases. On the contrary, when the zeta potential closes to zero, the nanofluids become easy to precipitate. As shown in Fig. 4, the zeta potential tends to decrease with increasing concentration of the nanoparticles, although the decrease is not significant. It is due to particle aggregation when the concentration of the nanoparticles is relatively high. Compared to the EG-Al$_2$O$_3$ nanofluid of Yashino [11], the zeta potential in this work is much larger almost twice. It may be due to small particle size and large specific surface area.
3.2.2. Viscosity
Viscosity is an important characteristic of heat transfer nanofluids. Figure 5 reveals the viscosity of the EG-Al$_2$O$_3$ nanofluids as function of temperature. The viscosity of all nanofluids as well as EG decreases with increasing temperature. The relationship between the viscosity and the temperature fits a model of equation (4). B is related to the free activation energy of fluid, and A is fitting parameter [16].

$$\eta = A \cdot \exp \left( \frac{B}{T} \right)$$

where, $\eta$ is the viscosity, A and B are constant, and $T$ is the temperature in Kelvin.

Figure 6 shows the viscosity of the nanofluids as function of Al$_2$O$_3$ concentration at temperature of 27°C. The present data is compared to Einstein model and model of Wang et al [9]. As clearly seen in Fig. 6, neither Einstein model nor model of Wang et al. does not fit the experimental data. This fact shows that the nanofluid is more complicated than the two phase fluid that used for Einstein model.

3.2.3. Critical Heat Flux (CHF)
Figure 7 depicts the data of CHF enhancement as function of concentration of Al$_2$O$_3$ nanoparticles. The CHF enhancement is defined as $[(\text{CHF}_{NF} - \text{CHF}_{EG})/\text{CHF}_{EG}] \times 100\%$. where, CHF$_{NF}$ is critical heat flux of the nanofluid, and CHF$_{EG}$ is critical heat flux of the ethylene glycol.
CHF in pool boiling is defined as the peak heat flux under which a boiling surface can sustain nucleate boiling. CHF is the end of nucleate boiling and means the limit of safe operation of a heat transfer system. The CHF is an important characteristic of the nanofluid other than viscosity and thermal conductivity. The understanding of CHF phenomenon is important for safe and economic design of many heat transfer units. A nanofluid with large CHF is required for the coolant applied in ECCS (Emergency Core Cooling System) dan RVCS (Reactor Vessel Cooling system), electronic coolant, refrigeration and cryogenic, and metal forming.

As shown in Fig.7, the CHF enhancement increases with the concentration of Al₂O₃ nanoparticles. The increase of the CHF enhancement reaches an optimal condition at the concentration of 0.095 vol % where the enhancement of 54% is the largest one. The enhancement of the CHF of the nanofluids is due to increasing surface area of the wire that interfaces with the nanofluid. The nanoparticles in the nanofluid are deposited on the surface of the wire, generating a porous layer with large surface area. Then, when the surface area of the wire increases, heat transfer from the wire to the nanofluid also increases, resulting in larger CHF. Compared to the CHF enhancement of Water-Al₂O₃ nanofluid with particle size 200-210 nm and concentration of 0.001-0.1 vol % using SS wire in literature [17] of 50%, the enhancement in this study is comparable. However, the enhancement is smaller compared to the CHF enhancement of Water-Al₂O₃ nanofluid with particle size 47 nm and concentration of 0.00001-0.1 vol % using Ni-Cr wire in literature [17] of 100%. Actually, the comparison is not fully true due to different base fluid and wire, and because pH of the nanofluids in literature [17] was not reported as well. Direct comparison to the CHF enhancement of the ethylene glycol-Al₂O₃ nanofluids could not be done due to lack of literature data especially the CHF data.

4. Conclusions
Nanoparticles of Al₂O₃ with crystallite size of 4.12 nm and specific surface area of 296.7 m²/gr have been successfully synthesized from local bauxite, and nanofluids of ethylene glycol (EG)-Al₂O₃ have been well prepared. The viscosity of the EG-Al₂O₃ nanofluids increases with the concentration of Al₂O₃ nanoparticles. The viscosity is also temperature dependent which decreases with increasing temperature. The CHF of the nanofluids is larger than that of ethylene glycol. The CHF enhancement of the nanofluids increases as the concentration of Al₂O₃ nanoparticles increases, and reaches the optimal value of 54% at the Al₂O₃ concentration of 0.095 vol %.

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6. References

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