Hydrothermally Synthesis of Al₂O₃ Nanoparticles for Nanofluids with Enhanced Critical Heat Flux

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Abstract. Water is widely used as a heat carrier in various devices such as automotive and nuclear reactors. Because of its better thermal characteristics, currently nanofluid is a candidate for replacing water and other conventional cooling fluids such as ethylene glycol and oil as a heat carrier. In this study, Al₂O₃ nanoparticles have been synthesized by the hydrothermal method for heat transfer nanofluid as an alternative to the new cooling fluid. Nanoparticles were synthesized using AlCl₃ as a precursor, and urea was used as a capping agent. The hydrothermal process was carried out at 175°C for 17 hours. The hydrothermal product was dried and then calcined at 500°C for 1 hour. The resulting Al₂O₃ nanoparticles were analyzed using XRD, FTIR, and TEM. Nanofluids were prepared from these nanoparticles by dispersing them into the water as a base fluid. Nanofluid characterization was carried out through Critical Heat Flux (CHF) measurements. According to the XRD data, the Al₂O₃ nanoparticles produced were gamma-alumina with a crystallite size of 4 nm. The BET specific surface area was 302 m²/g. From the TEM image, it was known that the nanoparticles formed a cluster of rod-shaped particles. FTIR data shows the presence of OH groups on the surface of the nanoparticles. The Al₂O₃ nanofluids made were known to be stable with an average zeta potential of 54 mV. Compared to water, the CHF enhancement of this nanofluid increased by 111%. The nanofluid has the potential to be used as a cooling fluid for ECCS, RVCS, refrigeration, and metal machining process.

Keywords: Nanoparticles, Al₂O₃, nanofluids, hydrothermal, urea, CHF.

1. Introduction

Conventional cooling fluids such as water have long been used in everyday life for heat carrier as can be found in industrial process heating and cooling systems, automotive, and nuclear reactors. With increasingly global competition, there is a strong need to increase the economic and safety level of various equipment that utilizes heat transfer systems. However, the inherent thermal conductivity of conventional fluids is small so that to realize this need a new fluid with better performance is required. One of the promising fluids as a substitute for the conventional cooling fluid is nanofluid. Nanofluids have higher thermal conductivity and critical heat flux (CHF) compared to the conventional cooling fluids [1-6].

Nanofluid was first coined by Choi from MIT, the United States in 1995 [1]. Nanofluid is the dispersion of nanoparticles with a size of 1-100 nm into base fluids such as water, ethylene glycol, and oil. The nanofluid can be made from various types of nanoparticles such as ZrO₂ [7, 8], ZnO [9], Fe₃O₄ [5], and Al₂O₃ [6]. Among the various types of nanoparticles, Al₂O₃ is very interesting because it has such advantages as low density, relatively large thermal conductivity, small coefficient of thermal neutron absorption [10], and the availability of large local raw materials. Low density and large thermal conductivity are needed for nanofluid. Meanwhile, the low coefficient of thermal neutron absorption is needed for nanofluid which will be applied in nuclear reactors.
The production of Al₂O₃ nanofluid has been carried out using Al₂O₃ nanoparticles synthesized by the method of precipitation [6], and sol-gel [11]. The thermal characteristics of the nanofluids were made quite well with CHF enhancement of 20-150% [12], but their stability still needs to be improved. The stability of the nanofluid is strongly influenced by the characteristics of the nanoparticles which are strongly influenced by the method of synthesis. In this study, the synthesis of Al₂O₃ nanoparticles by the hydrothermal method using urea as an additive or capping agent was carried out. Urea was used to create surface characteristics of Al₂O₃ nanoparticles suitable for nanofluid. As far as the author's knowledge, the synthesis of Al₂O₃ nanoparticles for nanofluid with this technique has not been reported.

2. Experiment
2.1 Materials and equipment
The materials used mainly were aluminum chloride, urea, and aquadest. While the main equipment used was hot plate magnetic stirrer, furnace, glassware, pH meter, zeta sizer, XRD, FTIR, TEM, and CHF measuring devices.

2.2 Synthesis and Characterization of Al₂O₃ nanoparticles
The process started with dissolving some AlCl₃ powder with water in a beaker glass. Then urea was put into the solution, with a weight ratio between AlCl₃ and urea was 1:2. The mixture was stirred with a magnetic stirrer. The homogeneous mixed solution was put into a Teflon lined SS autoclave. The autoclave was then put into the muffle furnace to be heated at 175°C for 17 hours. The product from the hydrothermal process was dried, and then calcined at a temperature of 400°C, 500°C, and 600°C for 2 hours. Calcined products were crushed to obtain Al₂O₃ nanoparticles. The nanoparticles were analyzed using an XRD to determine the crystal structure, crystallite size, and phases formed. The BET specific surface area of the nanoparticles was measured using a surface area meter from Quantachrome. Particle size was measured using TEM. In order to find out the functional group formed on the surface of the nanoparticles, an FTIR analysis was carried out.

2.3 Preparation and characterization of nanofluids
0.3 g of Al₂O₃ nanoparticles from each sample with different calcination temperatures were dispersed into 100 ml of distilled water to form a suspension. The obtained suspension was vibrated with ultrasonic waves using an ultrasonic bath device (ultrasonication) for 1 hour to form nanofluid. The pH and zeta potential of the nanofluids were measured using a pH meter from Mettler Toledo and Malvern zeta sizer, respectively. Critical heat flux (CHF) measurements were carried out using a measuring device with the working principle described in reference [6, 12].

3. Results and Discussion
3.1 Visual appearance and Al₂O₃ Nanoparticles characterization
The visual appearance of Al₂O₃ nanoparticles synthesized in this study is shown in Figure 1. The powder of Al₂O₃ nanoparticles appear pure white. The results of the analysis of Al₂O₃ nanoparticles are shown in Figure 2. The main diffraction peaks are seen at 2θ = 45.7° and 66.9°. The diffraction peaks appear broadly, indicating a very small particle size. The diffraction patterns obtained were compared with standard diffraction patterns from JCPDS. From the results of the comparison, it is known that the diffraction pattern of Al₂O₃ nanoparticles synthesized in the study is very much in accordance with the standard JCPDS diffraction pattern No. 29-0063 for γ-Al₂O₃. The diffraction peak at 2θ = 45.7° corresponds to the plane (400) and 2θ = 66.9° corresponds to the plane (440). The crystallite size of Al₂O₃ nanoparticles is 4 nm which was calculated using the Debye Scherrer equation (1) [13].
D = \frac{0.9\lambda}{\beta \cos \theta} \quad \text{.................................. (1)}

Where, $D$ is the crystallite size, $\lambda$ is the wavelength, $\beta$ is FWHM, and $\theta$ is diffraction angle.

Figure 1. The visual appearance of the synthesized Al$_2$O$_3$ nanoparticles.

Figure 2. XRD pattern of the Al$_2$O$_3$ nanoparticles.

Figure 3 depicts the TEM image of the Al$_2$O$_3$ nanoparticles. The nanoparticles form a cluster of rod-shaped particles with an average diameter of the rod is about 6 nm. The formation of the structure of the nanoparticle cluster consisting of these rods occurs during calcination of the product of the hydrothermal process which is strongly influenced by urea as a capping agent. The BET specific surface area of the nanoparticles is very large namely 302 m$^2$/g. The particle size calculated from this specific surface area is 5 nm as calculated using equation $d=\frac{6000}{(\rho \cdot As)}$ where $d$ is the particle size (nm), $\rho$ is the particle density (here is Al$_2$O$_3$) (g/cm$^3$), and $As$ is the specific surface area (m$^2$/g). Recapitulation of the Al$_2$O$_3$ characteristics is shown in Table 1.

Figure 3. The TEM image of the Al$_2$O$_3$ nanoparticles.

Figure 4. FTIR data of the Al$_2$O$_3$ nanoparticles.

Figure 4 shows the FTIR spectrum of Al$_2$O$_3$ nanoparticles synthesized in this work. Functional groups are usually identified at intervals of wave numbers 1500-4000 cm$^{-1}$. While the interval number 600-1500 cm$^{-1}$ is the fingerprint region. As shown in Figure 4, O-H bending vibration is found at around 1632 cm$^{-1}$, and the stretching vibration of surface adsorbed water and vibration bands from hydroxyl groups are identified on bands around 3447 cm$^{-1}$ [13, 14]. This data shows the presence of the number of hydroxyl groups on
the surface of alumina nanoparticles. As also found in Figure 4, the strong broadening band between 400-
1000 cm\(^{-1}\) for -Al-OH and –O-Al-O-Al– shows the characteristic vibration of Al\(_2\)O\(_3\). The presence of
functional groups such as seen in Figure 4 is also found in FTIR data in a work of Khazaei et al [14] and
our previous works [6, 11].

| No. | Characteristic         | Value                  |
|-----|------------------------|------------------------|
| 1   | Crystal structure      | \(\gamma\)-alumina     |
| 2   | Crystallite size       | 4 nm                   |
| 3   | Surface area           | 302 m\(^2\)/g          |
| 4   | BET particle size      | 5                      |
| 5   | Nanoparticle shape     | Cluster of rod-shaped particles |

Table 1. Characteristics of Al\(_2\)O\(_3\) nanoparticles.

3.2 Characterization of Al\(_2\)O\(_3\) Nanofluids
The visual appearance of Al\(_2\)O\(_3\) nanofluids is shown in Fig. 5. Zeta potential of the nanofluids was
measured using a zeta sizer at different observation times. The zeta potential as a function of observation
time is depicted in Fig. 6. The zeta potential is stable at an average value of 54 mV at least until 32 days of
observation time. The value is far from the border at a value of 30 mV. It is known that the nanofluid with
zeta potential larger than 30 mV is stable.

As one of the important characteristics of nanofluids, CHF was measured using equipment whose working
principle can be found in the literature [6, 12]. The CHF from the nanofluids made is relatively very large
compared to the CHF of water as the base fluid. The CHF enhancement obtained was 111% compared to
water. Compared to the CHF enhancement reported in the literature, the CHF enhancement in this work is
large enough as can be seen in Table 2. It is due to the good stability of the nanofluids. Recapitulation of
the characteristics of the Al\(_2\)O\(_3\) nanofluid in this work is depicted in Table 3.

![Figure 5. The visual appearance of the Al\(_2\)O\(_3\) nanofluids.](image)

![Figure 6. The zeta potential as a function of time.](image)
Table 2. CHF enhancement of some nanofluids.

| No. | Nanofluids | Heater type | CHF Enhancement (%) | Literature |
|-----|------------|-------------|---------------------|------------|
| 1   | Al₂O₃ in water, 0.001-0.025% g/L | Cu plate | 200 | [15] |
| 2   | Al₂O₃ (38nm) in water 0.037g/L | Ti layer on glass substrate | 67 | [15] |
| 3   | Al₂O₃ (10-100nm) in water 0.5-4v% | SS plate | 50 | [15] |
| 4   | TiO₂ (27-85nm) in water, 0.01-3v% | Cu plate | 50 | [15] |
| 5   | Au 4nm in water, 0.001-0.025% g/L | Cu plate | 175 | [15] |
| 9   | Al₂O₃ in water 0.3g/100 ml | Cu wire | 111 | This work |

Table 3. Characteristics of the Al₂O₃ nanofluid.

| No. | Characteristic | Value |
|-----|----------------|-------|
| 1   | Concentration  | 0.3g/100 ml |
| 2   | pH             | 5     |
| 3   | Zeta potential | 54 mV |
| 4   | CHF enhancement| 111 % |

Some applications such as Reactor Vessel Cooling System (RVCS) and Emergency Core Cooling System (ECCS) in Nuclear Reactors [16], metal machining [17], and refrigeration [18, 19] strongly require cooling fluids with large CHF. As explained in a literature, nanofluids can be applied in metal machining which includes drilling, turning, milling, and drilling. According to Shokoohi [17], cutting force, machining temperature, tool wear, and surface roughness can be reduced by applying nanofluids. The characteristics of nanofluids made in this study are quite good, so that these nanofluids have the prospect of being applied in metal machining metal processes too. In Bang and Kim's report [16] it is known that their nanofluid has a cooling rate (230°C/s) which is greater than the pure water cooling rate (218°C/s) and can be applied to RVCS and ECCS applications. With a relatively large CHF enhancement, the nanofluids prepared in this study are also possible to be applied in RVCS and ECCS.
4. Conclusion

Al$_2$O$_3$ nanoparticles with gamma crystal structure were successfully synthesized using the hydrothermal method with urea as a capping agent. The synthesized nanoparticles formed a cluster of rod-shaped particles with an average rod diameter of 6 nm. Al$_2$O$_3$ nanoparticles that are made can produce highly stable nanofluids with an average zeta potential of 54 mV. With large CHF enhancement of 111%, this nanofluid has the potential to be used as a cooling fluid for ECCS, RVCS, refrigeration, and metal machining process.

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Contribution Statement

The main contributor of this article is Dani Gustaman Syarif.

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